

(19)



Eur päisch s Pat ntamt
European Pat nt Office
Offi urop n d br v ts



(11)

EP 0 709 225 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
01.05.1996 Bulletin 1996/18

(51) Int Cl.⁶: **B41M 5/28, B41M 5/34**

(21) Application number: **95307663.5**

(22) Date of filing: **27.10.1995**

(84) Designated Contracting States:
BE DE FR GB IT SE

(30) Priority: **27.10.1994 JP 262998/94**
29.11.1994 JP 294142/94

(71) Applicant: **NIPPON PAPER INDUSTRIES CO., LTD.**
Kita-ku, Tokyo (JP)

(72) Inventors:
• **Minami, Toshiaki, c/o Res. Lab. of Product Dev.**
1-chome, Shinjuku-ku, Tokyo 161 (JP)

- **Nagai, Tomoaki, c/o Res. Lab. of Product Dev.**
1-chome, Shinjuku-ku, Tokyo 161 (JP)
- **Hamada, Kaoru, c/o Res. Lab. of Product Dev.**
1-chome, Shinjuku-ku, Tokyo 161 (JP)
- **Sekine, Akio, c/o Res. Lab. of Product Dev.**
1-chome, Shinjuku-ku, Tokyo 161 (JP)

(74) Representative: **Woods, Geoffrey Corlett**
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

(54) **Reversible multi-color thermal recording medium**

(57) A reversible multi-color thermal recording medium comprises, laminated on a substrate:

(i) an irreversible thermal composition comprising a colorless or pale basic achromatic dye and an organic irreversible heat-resistant color developer; and

(ii) a reversible multi-color thermal composition comprising a colorless or pale basic achromatic dye and an organic reversible heat-resistant color developer.

EP 0 709 225 A1

D scriptionBackground of the Invention

5 This invention relates to a reversible multi-color thermal recording medium which is free from color development of its ground when an image is formed or erased, has high sensitivity and provides a vivid color tone.

Thermal recording sheets are generally prepared by the following method. A colorless or pale basic achromatic dye and an organic developer made from a phenolic substance or the like are ground into fine particles and dispersed, and the resulting dispersions are mixed together. To the resultant mixture are added a binder, a filler, a sensitizer, a
 10 lubricant and other auxiliaries to prepare a coating fluid. The coating fluid is applied to a support such as paper, synthetic paper, film, plastic or the like to produce a thermal recording sheet. Color development recording is effected by an instantaneous chemical reaction caused by heating with a hot pen, a thermal head, a hot stamp, a laser beam or the like.

These thermal recording sheets are now applied in a wide range of fields such as measuring recorders, terminal printers for computers, facsimiles, automatic ticket vending machines, bar code labels and the like. Along with recent
 15 progress in the diversification and the improvement of performance of these recording apparatuses, higher quality is required for the thermal recording sheets. For instance, along with an increase in the speed of recording, the thermal recording sheets are required to obtain high-density and clear color images with extremely small heat energy. Further, the thermal recording sheets are required to be excellent in keeping quality such as light resistance, weather resistance and oil resistance.

20 On the other hand, due to a sharp increase in the consumption of information recording media resulted by the construction of a variety of networks and the popularization of facsimiles and copiers, waste disposal is becoming a social problem. As one of solutions to this problem, much attention is paid to recording media having reversibility, that is, so-called reversible recording media which allow for repetitions of recording and erasure.

The reversible recording media have been disclosed such as recording media in which a recording material changes
 25 between transparent and opaque reversibly according to given temperature, recording media which make use of reversibility of a thermochromic material, recording media which make use of reversible changes in the color tone of a leuco dye, and the like.

The reversible recording media in which a recording material changes between transparent and opaque reversibly are disclosed in Japanese Patent Publication Nos. 54-119377, 63-39377, 63-41186, 3-230993 and 4-366682. However,
 30 these reversible recording media have such defects as lack of image sharpness, slow decolorization speed and need for temperature control upon erasure.

The reversible recording media making use of a thermochromic material involve the problem that most of thermochromic materials have poor data storage ability and require continuous heat supply to keep color development.

Meanwhile, the reversible recording media making use of reversible changes in the color tone of a leuco dye are
 35 disclosed in Japanese Patent Publication Nos. 60-193691, 60-257289 and the like. However, these recording media effect decolorization with water or steam and have problems with practical application. Further, Japanese Patent Publication Nos. 2-188293 and 2-188294 disclose a simple layer-structured material (color developing and subtracting agent) which has both color developing and subtracting functions to provide reversible changes in the color tone of a leuco dye only by controlling heat energy. However, with this color developing and subtracting agent, satisfactory color
 40 density cannot be obtained because decolorization process already starts in process of color development. Further, decolorization cannot be accomplished. For this reason, satisfactory image contrast cannot be obtained.

A heated roll which is controlled to a specific temperature is used to erase an image on a reversible recording medium making use of reversible changes in the color tone of a leuco dye. Since a reversible developer used in the reversible recording medium has no heat resistance, the ground of the medium markedly develops a color through
 45 heated roll treatment.

As described above, the reversible recording media of the prior art which make use of a reaction between a color coupler and a color developer involve various problems and are still unsatisfactory.

Meanwhile, there have been great needs for multi-color recording media, and double-color thermal recording paper for use in labels, coupon tickets, video printers and the like has been implemented. This thermal recording paper is
 50 structured such that it is a laminate consisting of a support and high-temperature and low-temperature color developing layers formed on the support which develop colors with different color developing energies and two different methods have been proposed. One of them is to obtain a color of an image obtained when the high-temperature color developing layer develops a color as an intermediate color between a color developed only by the high-temperature layer and a color developed only by the low-temperature layer without discoloring an image of the low-temperature color-developing layer which develops a color when the high-temperature color developing layer develops a color. In this case, a double-
 55 color image having good contrast cannot be obtained unless a color developed by the high-temperature color developing layer can conceal a color developed by the high-temperature color developing layer thoroughly. It is impossible to form a double-color image if a color developed by the low-temperature color developing layer is black.

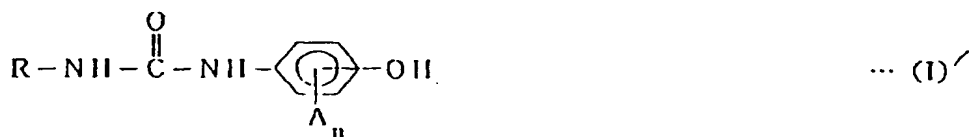
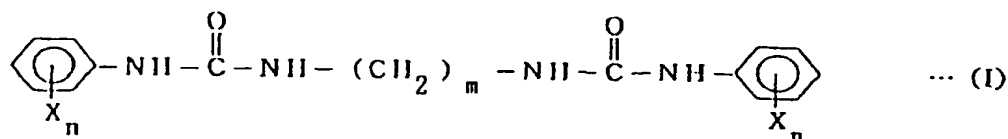
Another method is to erase a colored image of the low-temperature color developing layer which develops a color simultaneously with the color development of the high-temperature color developing layer, using an appropriate decolorizing agent. In this case, combinations of developed colors are arbitrary. However, since compatibility between color developing property and decolorization property is hard to be obtained, a satisfactory decolorization agent is yet to be discovered.

Summary of the Invention

It is therefore an object of the invention to provide a reversible multi-color thermal recording medium which is free from color development of its ground when an image is formed or erased, has high sensitivity, and provides a vivid color tone.

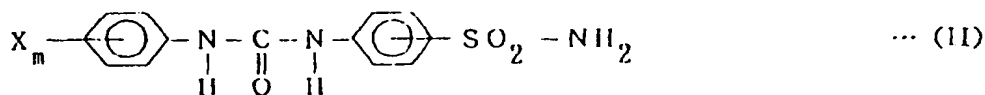
This invention has been made to solve the above problems by using an irreversible heat-resistant color developer as an organic color developer contained in an irreversible thermal composition and a reversible heat-resistant color developer as an organic color developer contained in a reversible thermal composition in a reversible multi-color thermal recording medium prepared by laminating the irreversible thermal composition containing a colorless or pale basic achromatic dye and the organic color developer as main components and the reversible thermal composition containing a colorless or pale basic achromatic dye and the organic developer as main components on a support.

In concrete terms, a compound represented by the following general formula (I) or (I') is used as the reversible heat-resistant color developer and at least one of compounds represented by the following general formulae (II), (III), (IV) and (V) is used as the irreversible heat-resistant color developer.

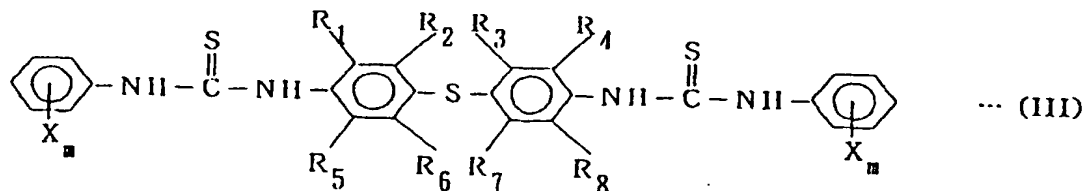


In the above formula (I), X is selected from the group consisting of a hydrogen atom, alkyl group having 1 to 12 carbon atoms, halogenated alkyl group having 1 to 3 carbon atoms, alkoxy group having 1 to 12 carbon atoms, alkoxycarbonyl group having 1 to 12 carbon atoms, acyl group having 1 to 12 carbon atoms, dialkylamino group having 1 to 12 carbon atoms, nitro group, cyano group and halogen atom, m is an integer of 1 to 12, and n is an integer of 1 to 3.

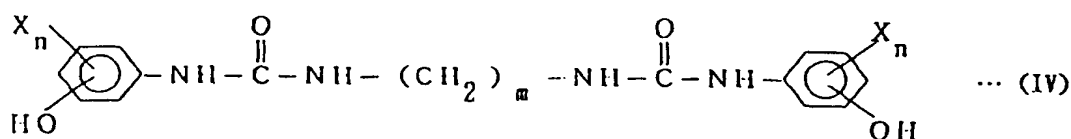
In the above formula (I'), R is an alkyl group having 12 to 22 carbon atoms, A is selected from the group consisting of a lower alkyl group, lower alkoxy group, lower alkoxycarbonyl group, nitro group, halogen atom and hydrogen atom, and n is an integer of 1 to 3.



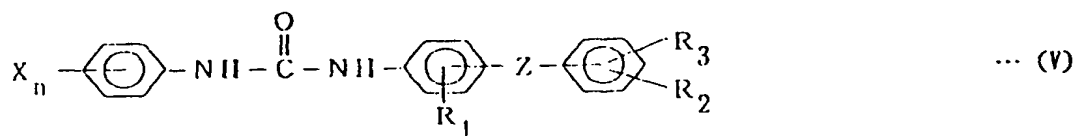
In the above formula, X is selected from the group consisting of a lower alkyl group having 1 to 4 carbon atoms, alkoxy group having 1 to 3 carbon atoms, hydrogen atom, nitro group, cyano group and halogen atom, and m is an integer of 1 to 3.



In the above formula, X, R₁, R₂, R₃, R₄, R₅, R₆, R₇ and R₈ are independently selected from the group consisting of a lower alkyl group having 1 to 6 carbon atoms, alkoxy group having 1 to 6 carbon atoms, hydrogen atom, nitro group, cyano group and halogen atom, and m is an integer of 1 to 3.



in the above formula, X is selected from the group consisting of a lower alkyl group having 1 to 6 carbon atoms, alkoxy group having 1 to 6 carbon atoms, nitro group, halogen atom and hydrogen atom, m is an integer of 1 to 12, and n is an integer of 1 or 2.



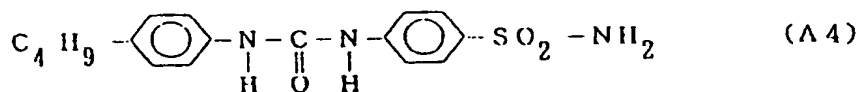
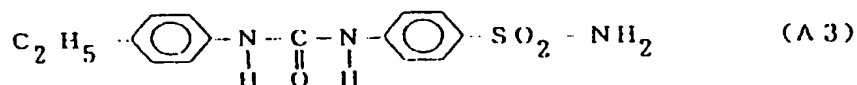
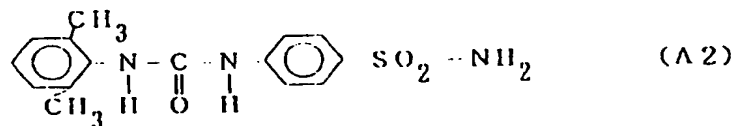
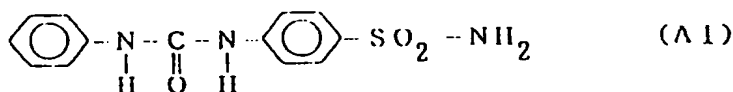
In the above formula, X is selected from the group consisting of an alkyl group having 1 to 12 carbon atoms, alkoxy group having 1 to 12 carbon atoms, trihalogenated methyl group, hydrogen atom, nitro group and halogen atom, Z is selected from the group consisting of O, S, straight chain having 1 to 12 carbon atoms, branched alkylene group, NH, SO₂ and C=O, R₁, R₂ and R₃ are independently selected from the group consisting of an alkyl group having 1 to 6 carbon atoms, hydrogen atom, nitro group and halogen atom, and n is an integer of 1 to 3.

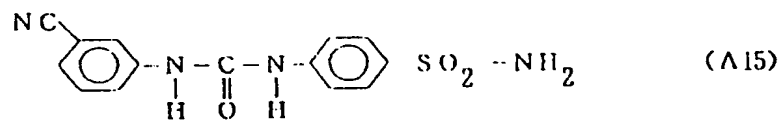
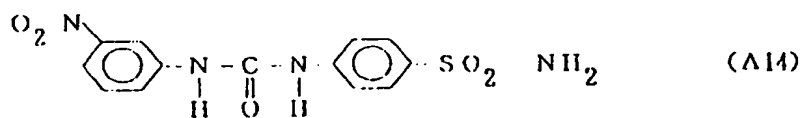
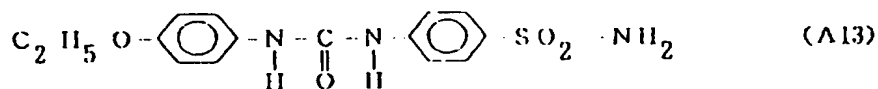
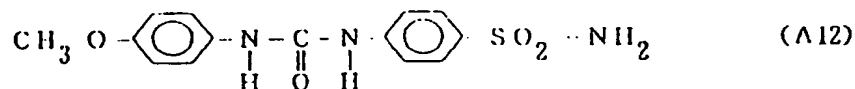
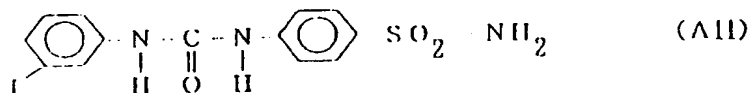
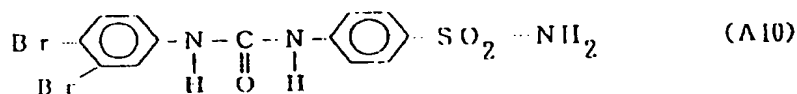
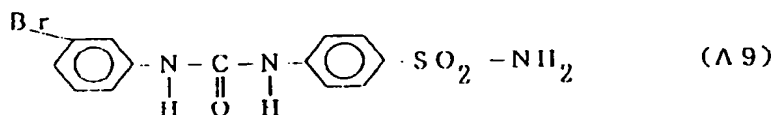
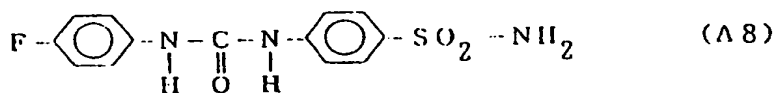
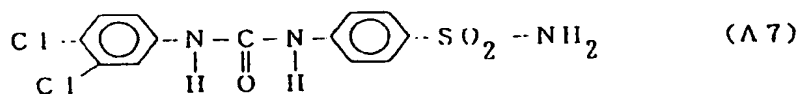
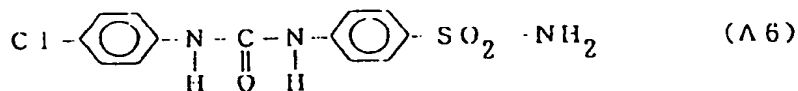
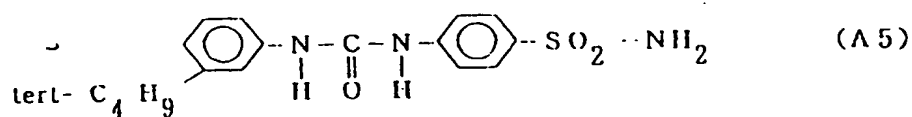
As for erasure of an image on the reversible thermal recording medium, various methods are conceivable such as one in which temperature and the amount of heat lower than those at the time of recording are given with a thermal head, a hot stamp, a heated roll or the like for erasure, one in which the amount of light smaller than that at the time of recording is irradiated by a laser, a halogen lamp or the like for erasure, and one in which the ground of a recording medium is brought into contact with a low-boiling alcohol solvent such as methanol and ethanol for erasure. Particularly, a heated roll controlled to 100 to 150 °C is easily used from a view point of operational ease. In this case, since the reversible recording composition and the irreversible recording composition are treated with a heated roll at the same time, a heat-resistant color developer needs to be used to prevent both of the reversible recording composition and the irreversible recording composition from developing colors from their grounds.

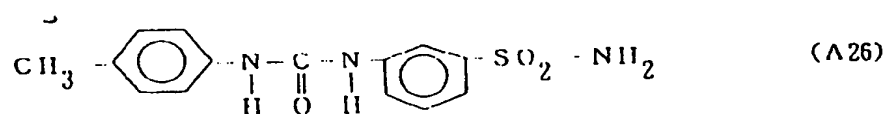
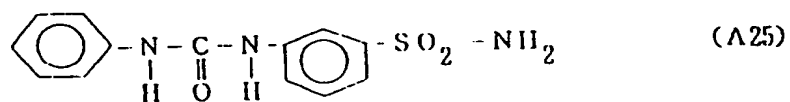
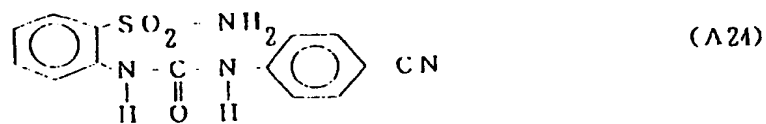
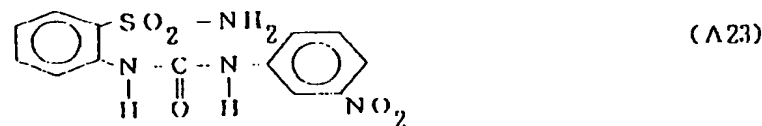
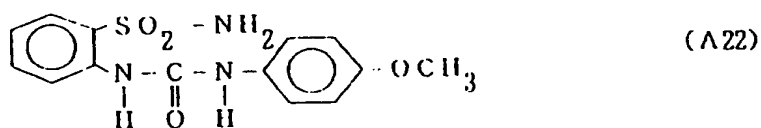
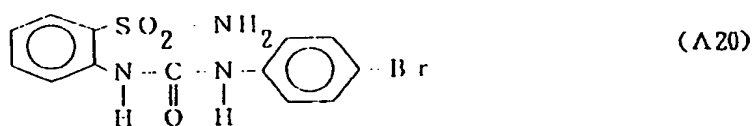
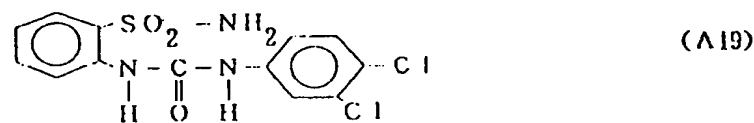
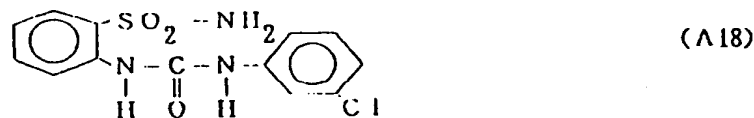
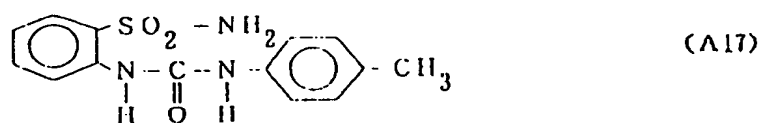
Further, as for the order of laminating the reversible recording composition and the irreversible recording composition onto a support, the support, the irreversible recording composition and the reversible recording composition may be laminated in the order named, or the support, the reversible recording composition and the irreversible recording composition may be laminated in the order named. Or two or more layers of the reversible recording composition and the irreversible recording composition may be laminated together.

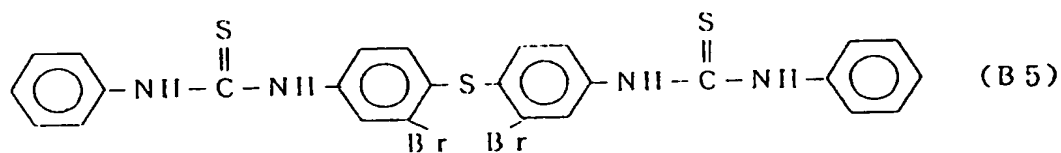
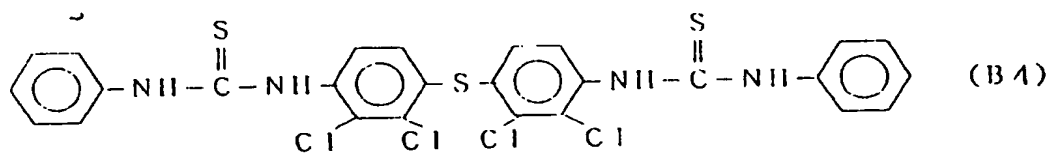
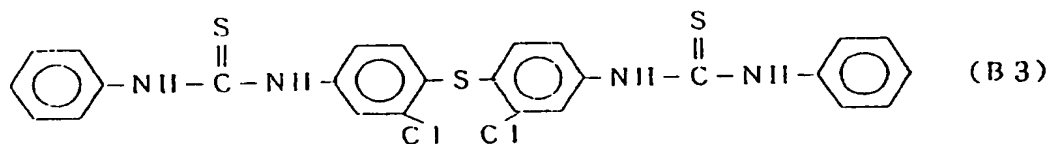
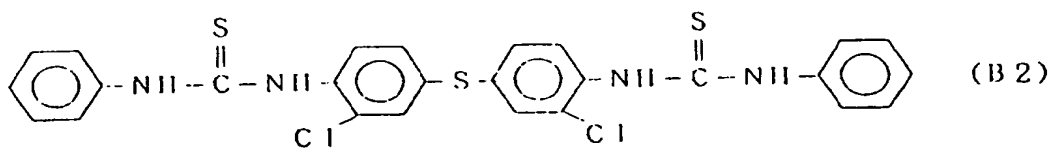
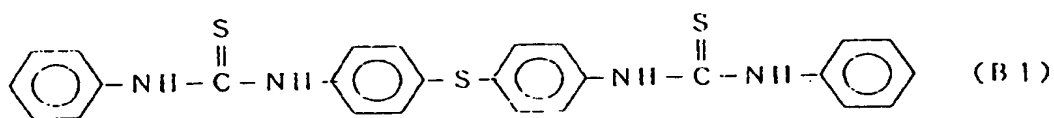
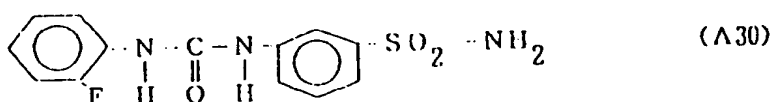
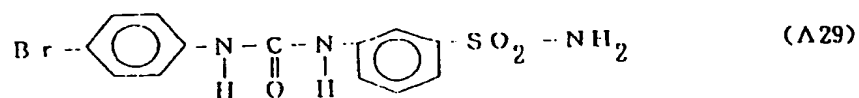
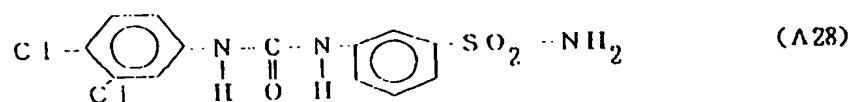
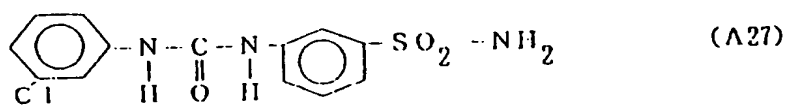
In the present invention, since the hue of an image obtained by first recording or erasure is made different from the hue of an image recorded next by using a combination of the irreversible recording composition and the reversible recording composition, it is possible to find whether an recorded image is additionally recorded or not.

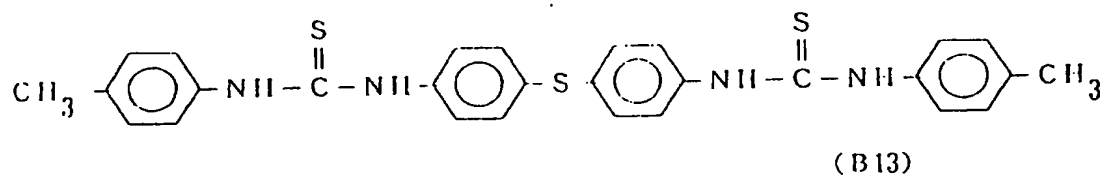
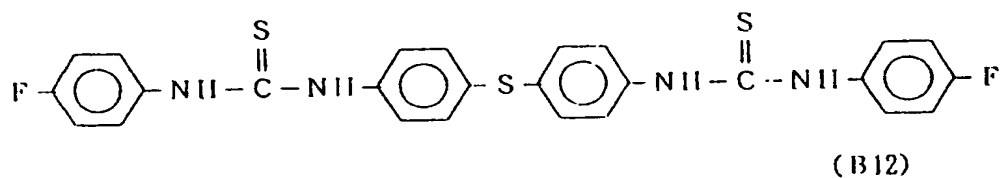
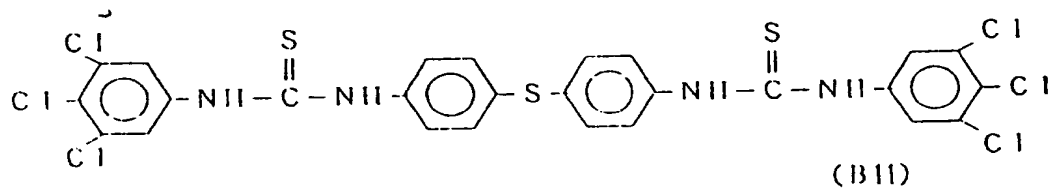
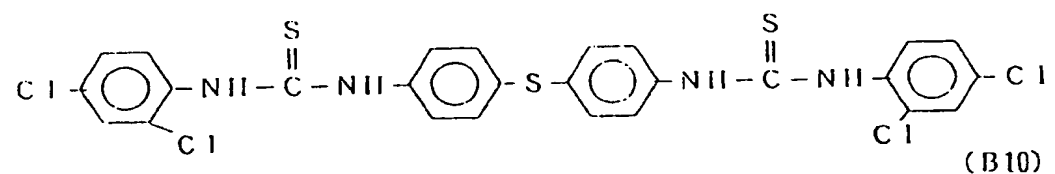
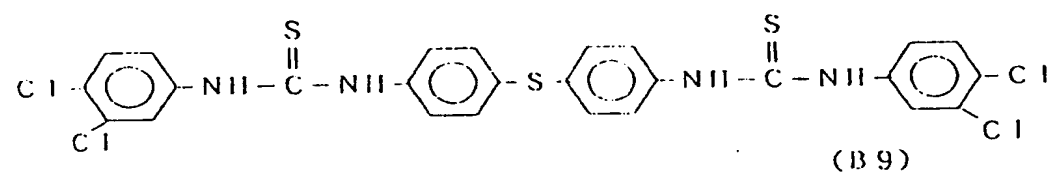
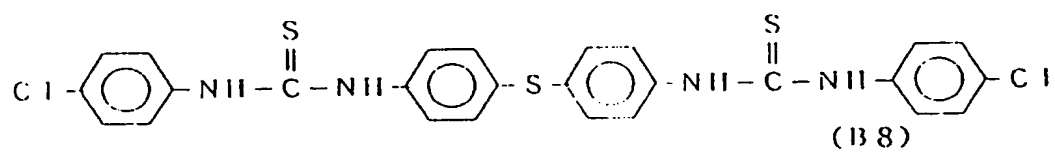
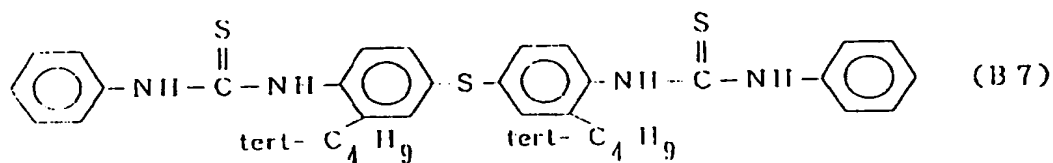
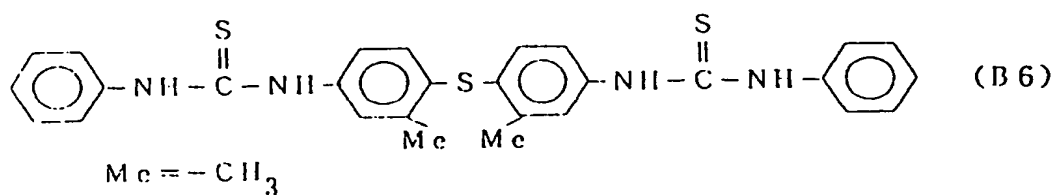
Illustrative examples of the irreversible heat-resistant color developer used in combination with the leuco dye in the reversible multi-color thermal recording medium of the present invention include the following urea compounds and thiourea compounds. However, the color developer of the present invention is not limited to these.

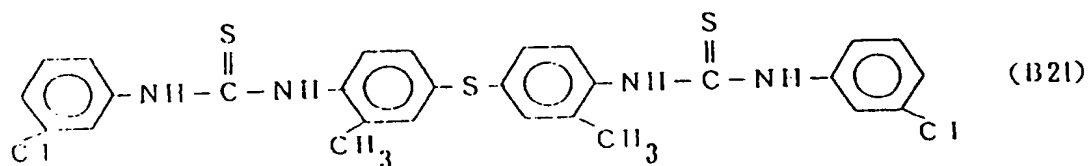
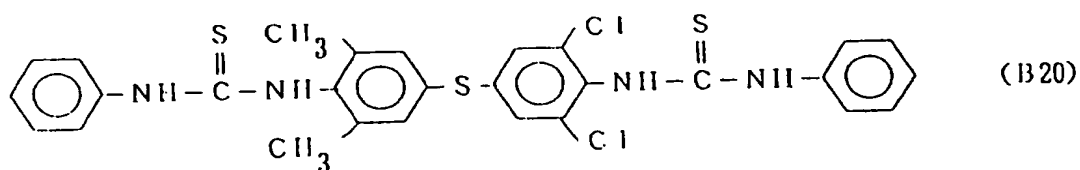
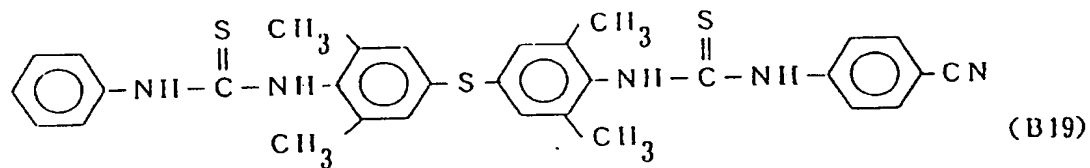
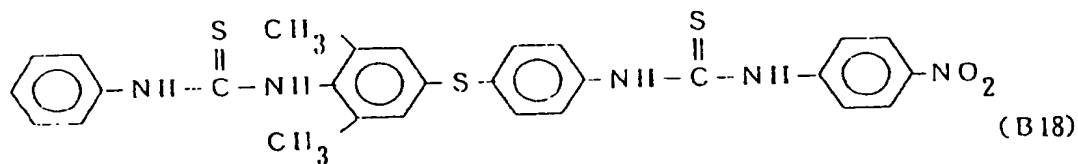
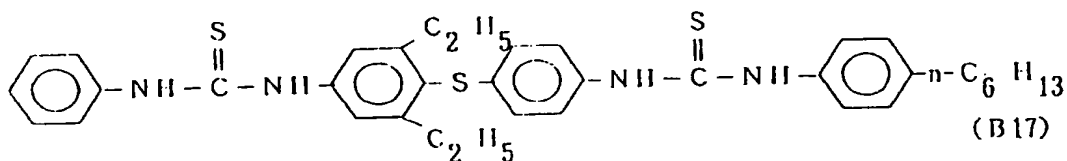
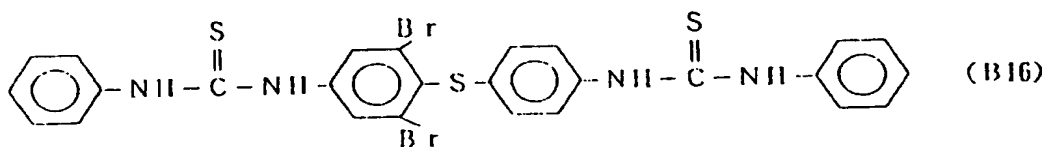
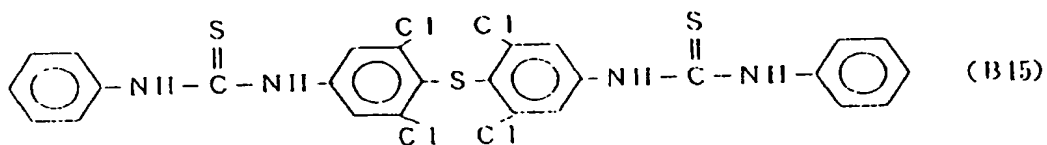
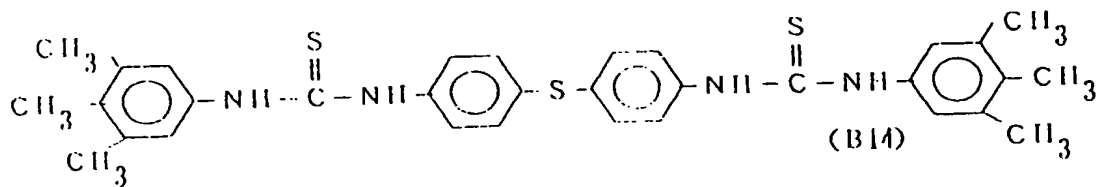


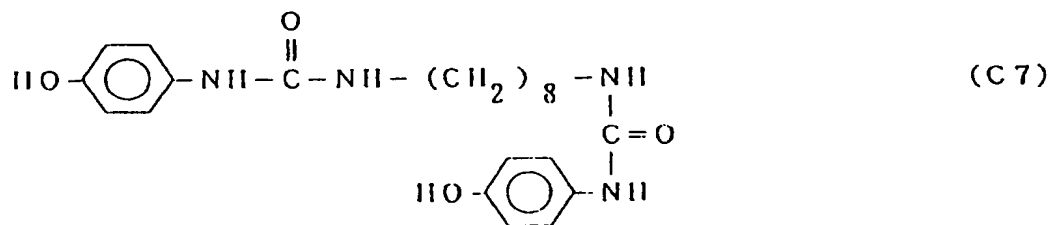
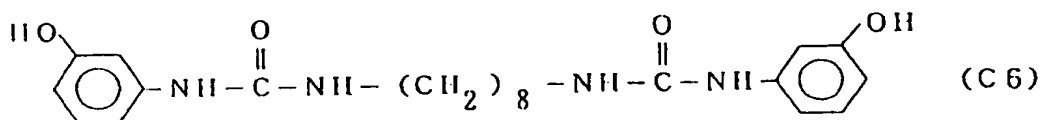
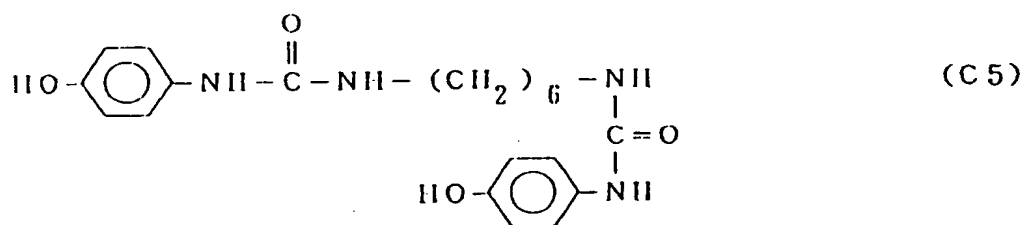
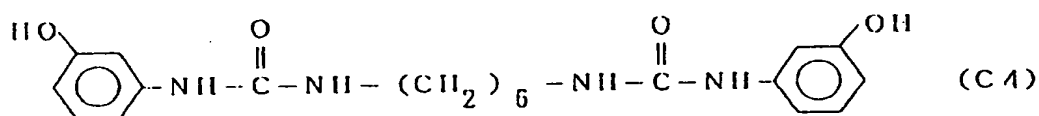
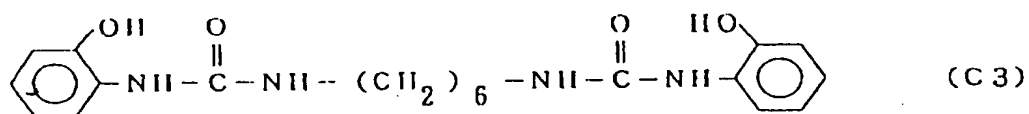
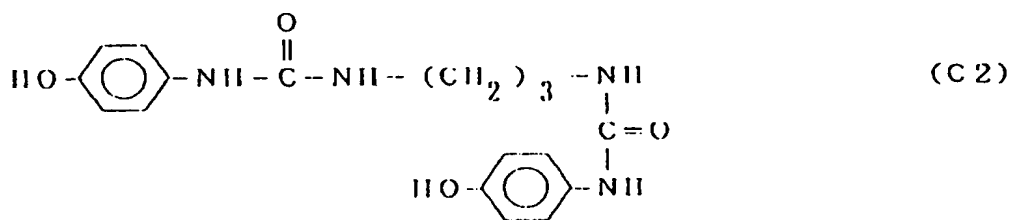
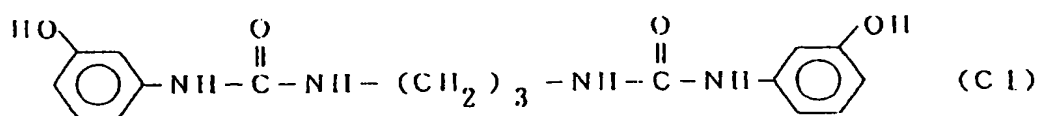


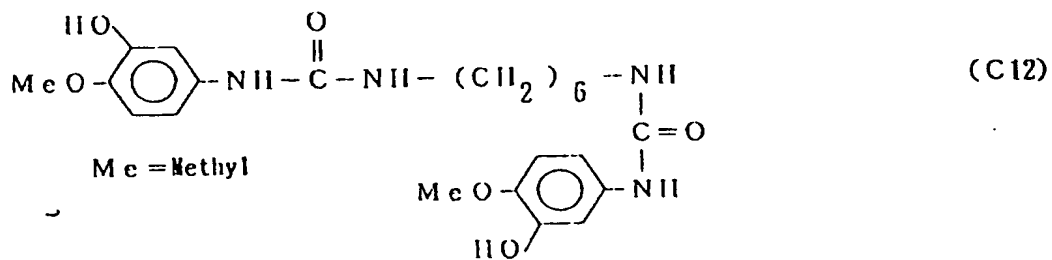
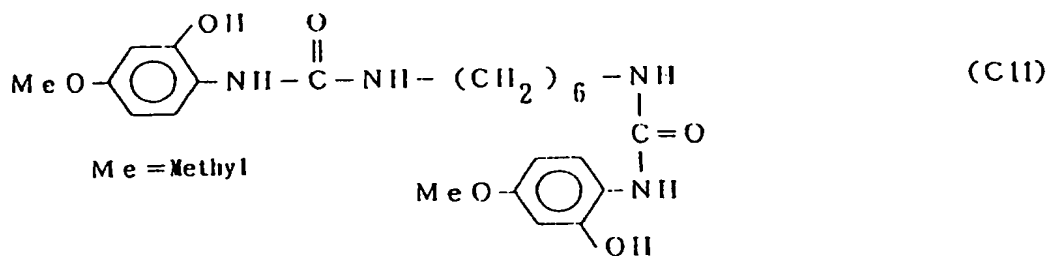
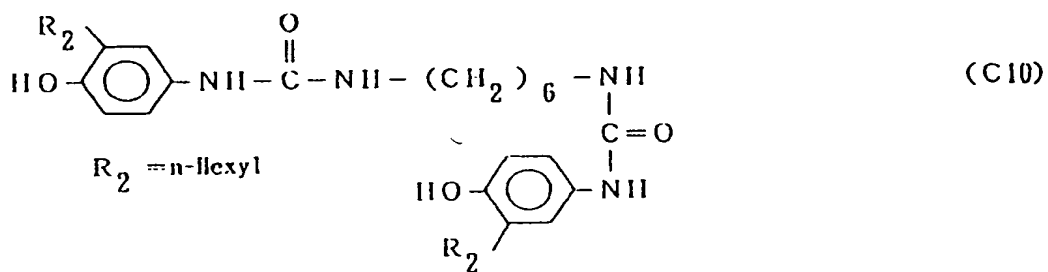
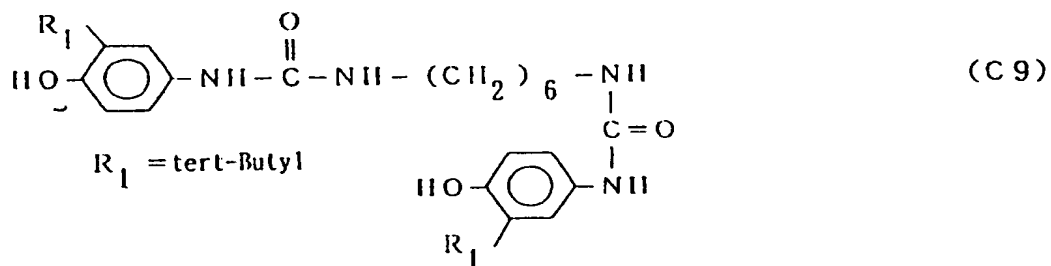
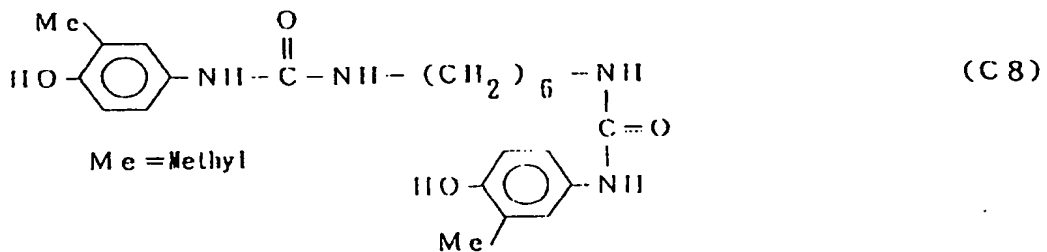


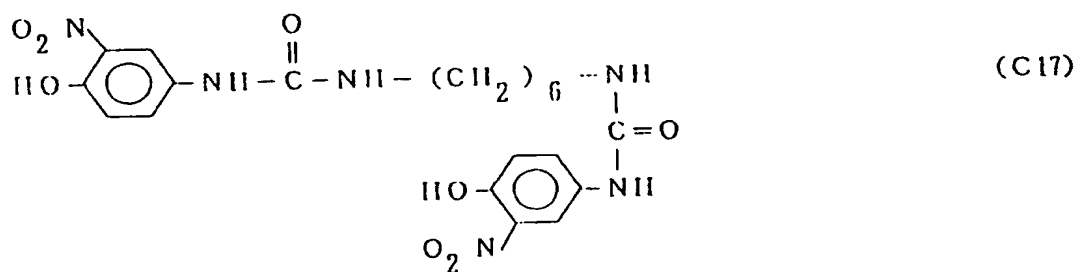
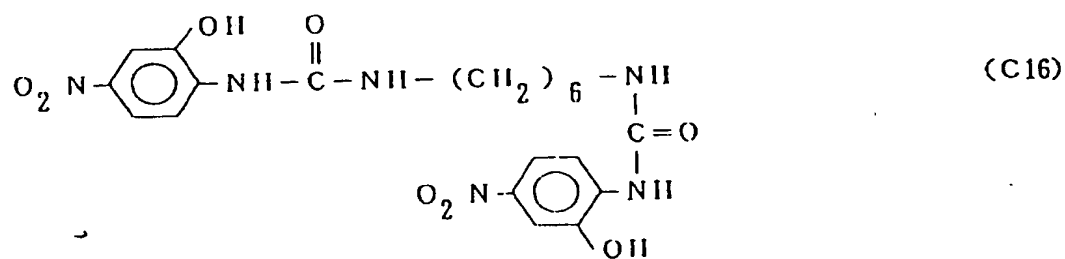
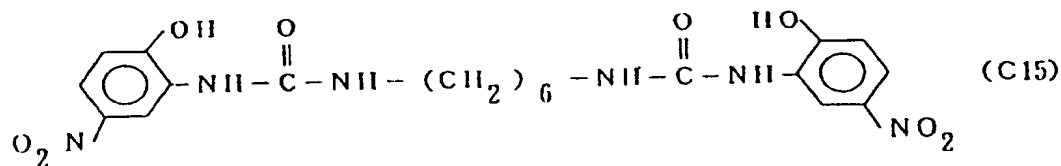
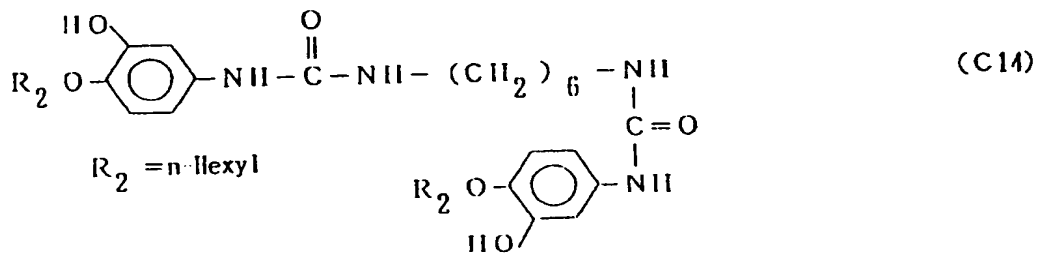
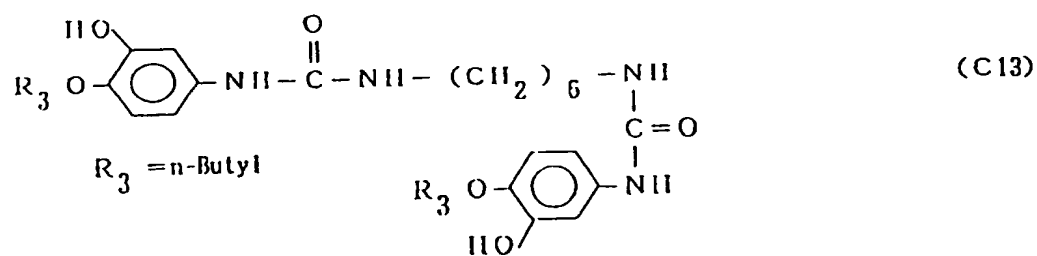


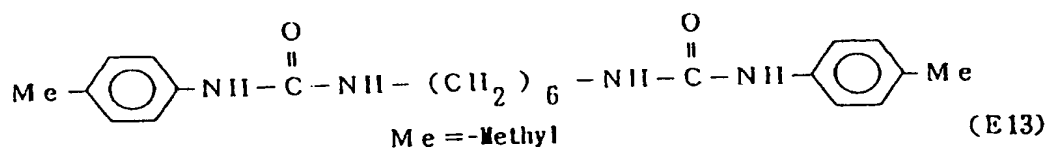
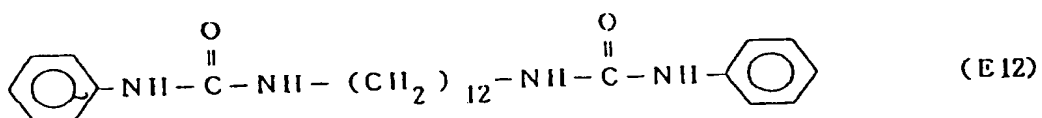
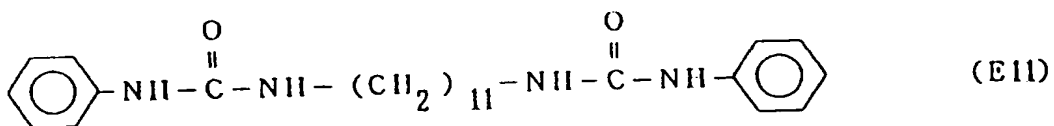
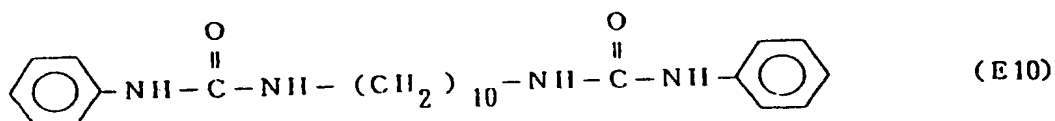
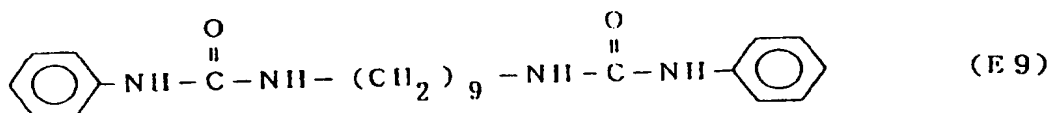
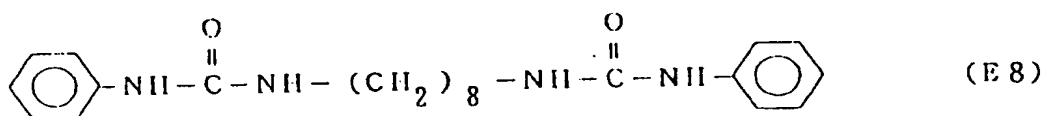
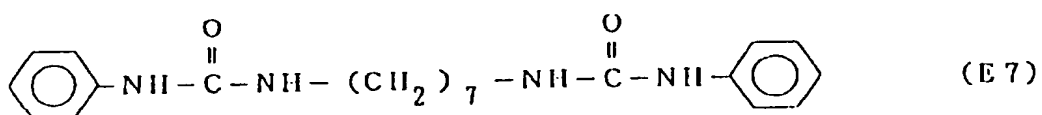
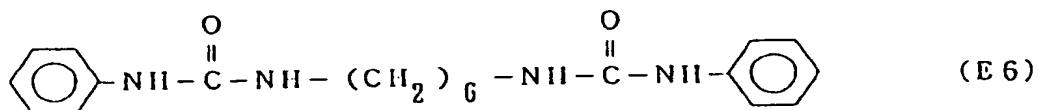
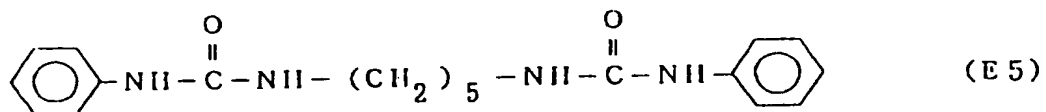
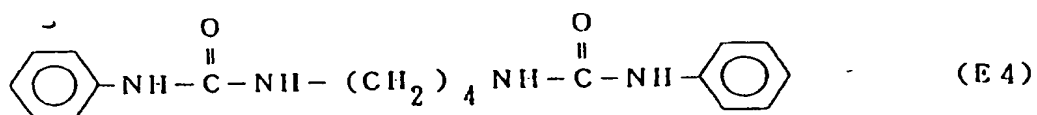


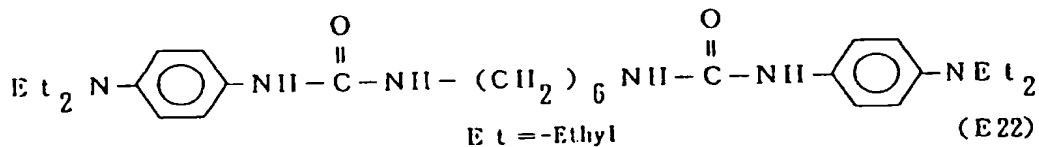
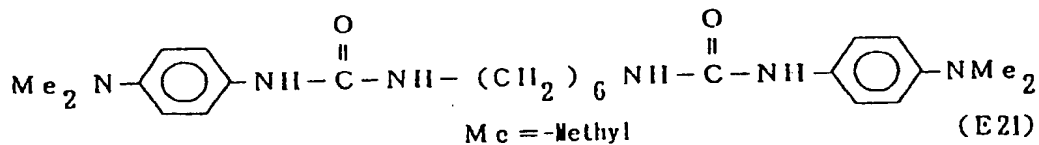
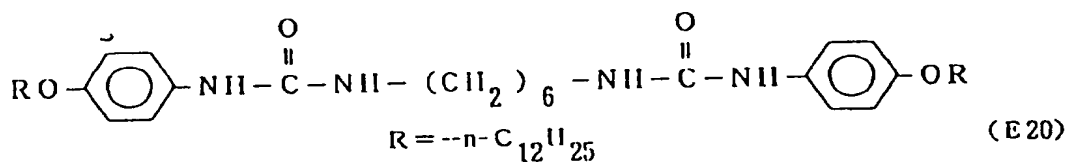
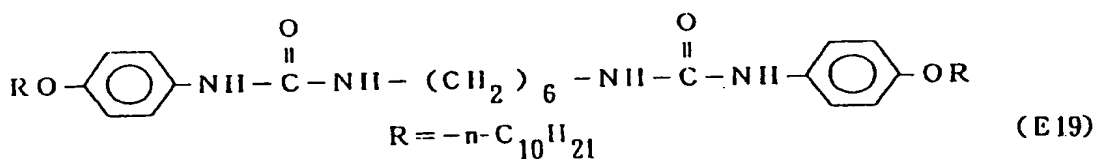
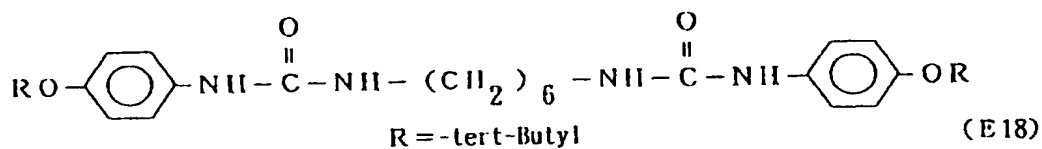
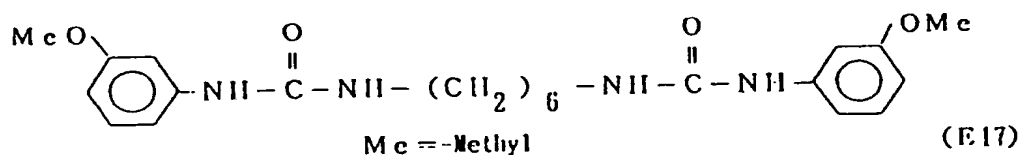
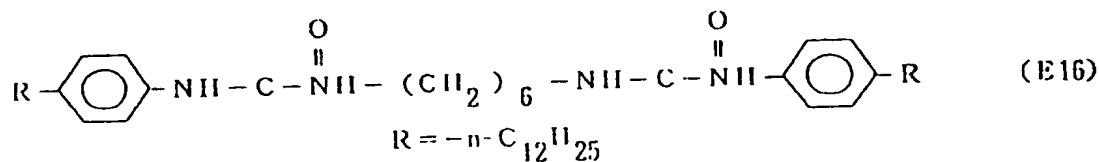
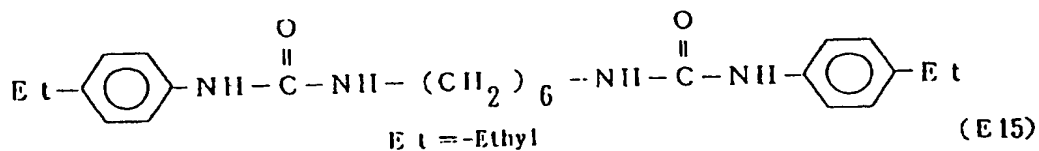
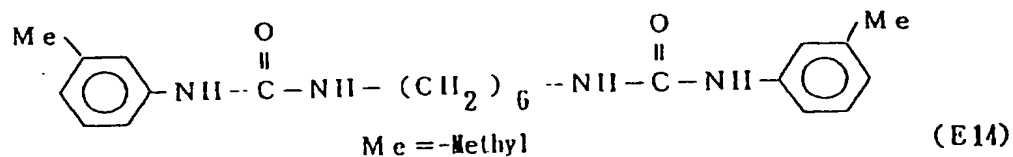


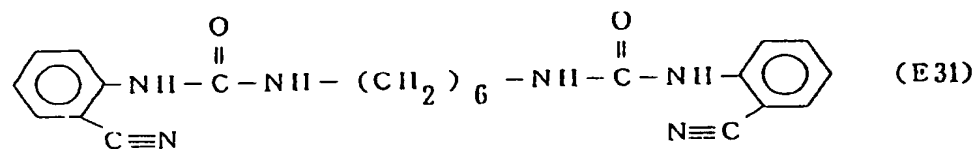
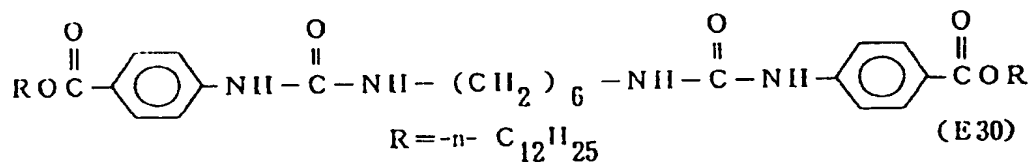
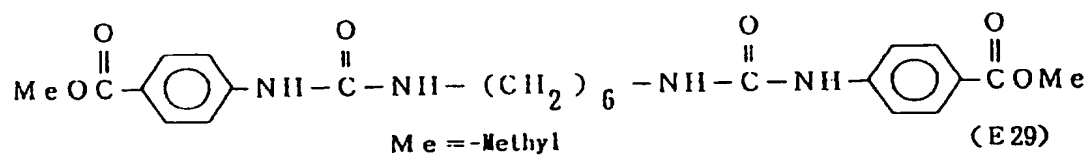
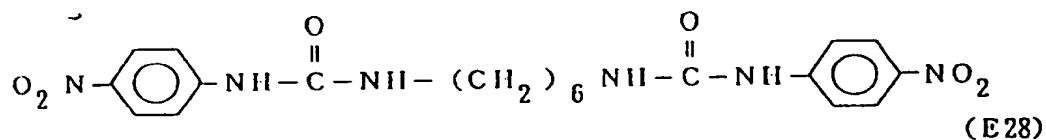
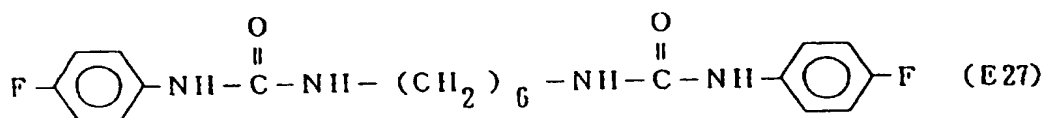
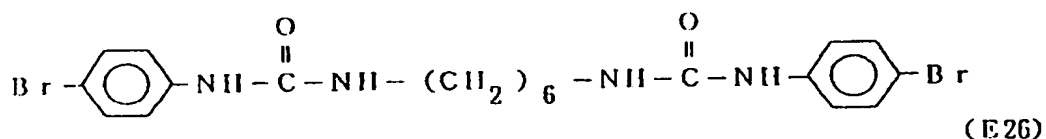
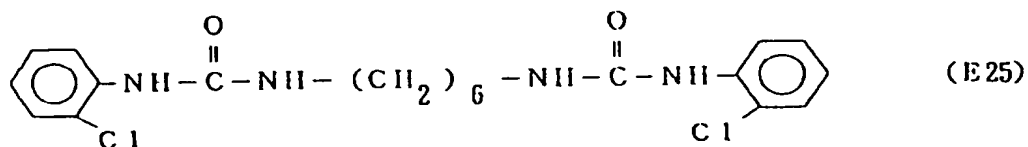
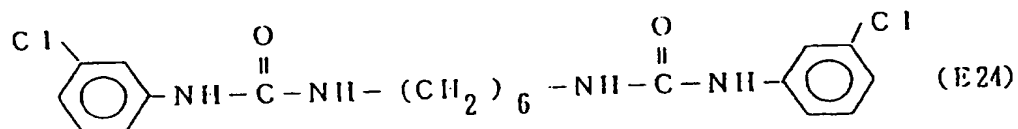
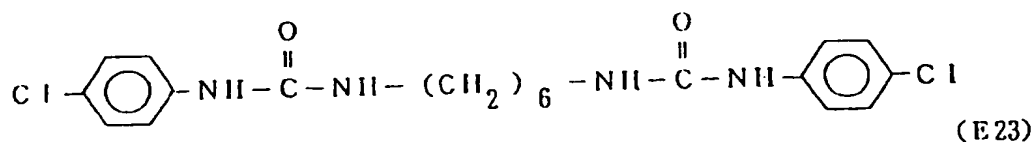


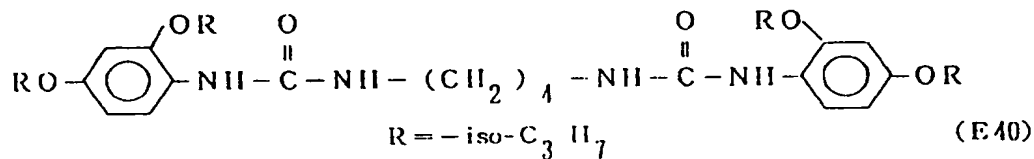
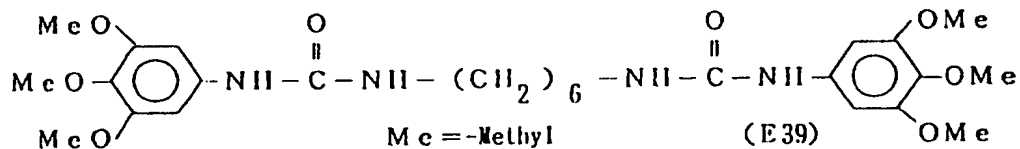
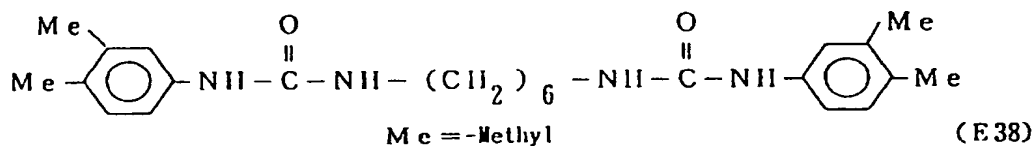
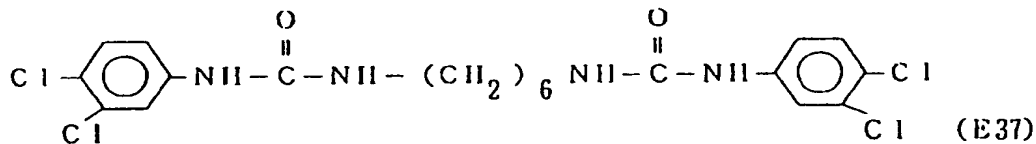
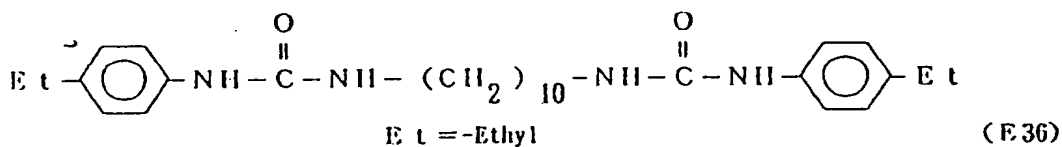
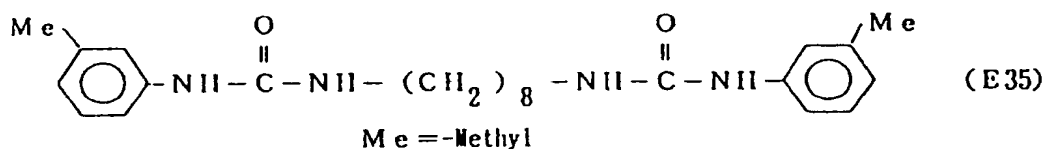
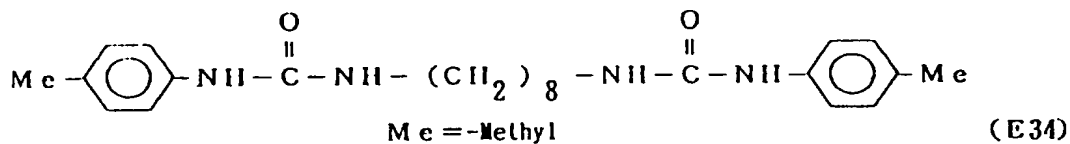
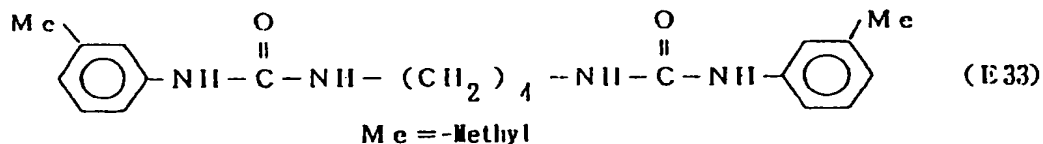
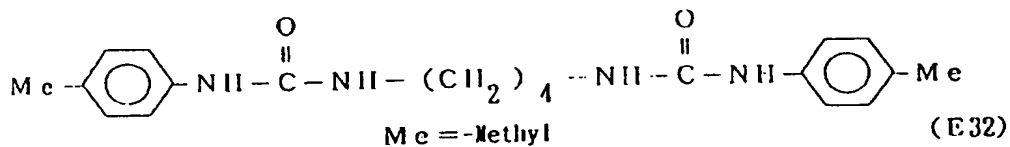












55 In the reversible multi-color thermal recording medium of the present invention, illustrative examples of the reversible heat-resistant color developer used in combination with the leuco dye include the following compounds represented by the general formula (I').

N-octadecyl-N'-(4-hydroxyphenyl) urea (E1')
 N-octadecyl-N'-(3-hydroxyphenyl) urea (E2')
 N-octadecyl-N'-(2-hydroxyphenyl)urea (E3')
 N-octadecyl-N'-(4-hydroxy-2-methylphenyl) urea (E4')
 5 N-octadecyl-N'-(2-hydroxy-4-methylphenyl) urea (E5')
 N-octadecyl-N'-(4-hydroxy-2-nitrophenyl)urea (E6')
 N-octadecyl-N'-(4-hydroxy-3-nitrophenyl)urea (E7')
 N-octadecyl-N'-(3-hydroxy-4-methoxyphenyl)urea (E8')
 N-octadecyl-N'-(5-hydroxy-2-methoxyphenyl) urea (E9')
 10 N-octadecyl-N'-(4-chloro-2-hydroxyphenyl) urea (E10')
 N-octadecyl-N'-(3-chloro-4-hydroxy-5-methylphenyl)urea (E11')
 N-octadecyl-N'-(3, 5-dichloro-4-hydroxyphenyl) urea (E12')
 N-octadecyl-N'-(3,5-dibromo-4-hydroxyphenyl)urea (E13')
 N-dodecyl-N'-(4-hydroxyphenyl) urea (E14')
 15 N-dodecyl-N'-(3-hydroxyphenyl)urea (E15')
 N-dodecyl-N'-(2-hydroxyphenyl) urea (E16')
 N-dodecyl-N'-(4-hydroxy-2-methylphenyl)urea (E17')
 N-dodecyl-N'-(4-hydroxy-3-nitrophenyl)urea (E18')
 N-dodecyl-N'-(3-hydroxy-4-methoxyphenyl)urea (E19')
 20 N-dodecyl-N'-(3-chloro-4-hydroxy-5-methylphenyl)urea (E20')
 N-dodecyl-N'-(3,5-dichloro-4-hydroxyphenyl)urea (E21')
 N-tetradecyl-N'-(4-hydroxyphenyl)urea (E22')
 N-tetradecyl-N'-(3-hydroxyphenyl) urea (E23')
 N-tetradecyl-N'-(2-hydroxyphenyl) urea (E24')
 25 N-tetradecyl-N'-(4-hydroxy-2-methylphenyl) urea (E25')
 N-tetradecyl-N'-(4-hydroxy-2-nitrophenyl) urea (E26')
 N-tetradecyl-N'-(5-hydroxy-2-methoxyphenyl) urea (E27')
 N-tetradecyl-N'-(3, 5-dibromo-4-hydroxyphenyl) urea (E28')
 N-hexadecyl-N'-(4-hydroxyphenyl) urea (E29')
 30 N-hexadecyl-N'-(3-hydroxyphenyl) urea (E30')
 N-hexadecyl-N'-(2-hydroxyphenyl)urea (E31')
 N-hexadecyl-N'-(4-hydroxy-2-methylphenyl) urea (E32')
 N-hexadecyl-N'-(4-hydroxy-2-nitrophenyl)urea (E33')
 N-hexadecyl-N'-(5-hydroxy-2-methoxyphenyl) urea (E34')
 35 N-hexadecyl-N'-(4-chloro-2-hydroxyphenyl) urea (E35')
 N-hexadecyl-N'-(3-chloro-4-hydroxy-5-methylphenyl)urea (E36')
 N-eicosyl-N'-(4-hydroxyphenyl) urea (E37')
 N-eicosyl-N'-(3-hydroxyphenyl) urea (E38')
 N-eicosyl-N'-(2-hydroxyphenyl) urea (E39')
 40 N-eicosyl-N'-(4-hydroxy-2-methylphenyl) urea (E40')
 N-eicosyl-N'-(4-hydroxy-2-nitrophenyl)urea (E41')
 N-eicosyl-N'-(5-hydroxy-2-methoxyphenyl) urea (E42')
 N-eicosyl-N'-(4-chloro-2-hydroxyphenyl) urea (E43')
 N-eicosyl-N'-(3-chloro-4-hydroxy-5-methylphenyl)urea (E44')
 45

In the reversible multi-color thermal recording medium of the present invention, the basic achromatic dye used in combination with the heat-resistant color developer is not limited to a particular kind, but triphenyl methane, fluoran, fluorene and divinyl-based dyes are preferred. Specific examples of these dyes are shown below. These dyes may be used alone or in combination of two or more.

<triphenylmethane-based leuco dyes>

3,3-bis(p-dimethylaminophenyl)-6-dimethylamino phthalid

5 [another name is crystal violet lactone]

<fluoran-based leuco dyes (I)>

10 3-diethylamino-6-methyl-7-anilino-fluoran
 3-(N-ethyl-p-toluidino)-6-methyl-7-anilino-fluoran
 3-(N-ethyl-N-isoamylamino)-6-methyl-7-anilino-fluoran
 3-diethylamino-6-methyl-7-(o,p-dimethylanilino) fluoran
 3-pyrrolidino-6-methyl-7-anilino-fluoran
 3-piperidino-6-methyl-7-anilino-fluoran
 15 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-anilino-fluoran
 3-diethylamino-7-(m-trifluoromethylanilino) fluoran
 3-N-n-dibutylamino-6-methyl-7-anilino-fluoran
 3-N-n-dibutylamino-7-(o-chloroanilino)fluoran
 3-(N-ethyl-N-tetrahydrofurfurylamino)-6-methyl-7-anilino-fluoran
 20 3-dibutylamino-6-methyl-7-(o,p-dimethylanilino) fluoran
 3-(N-methyl-N-propylamino)-6-methyl-7-anilino-fluoran
 3-diethylamino-6-chloro-7-anilino-fluoran
 3-dibutylamino-7-(o-chloroanilino) fluoran
 3-diethylamino-7-(o-chloroanilino) fluoran
 25 3-diethylamino-6-methyl-chloro-fluoran
 3-diethylamino-6-methyl-fluoran
 3-cyclohexylamino-6-chloro-fluoran
 3-diethylamino-benzo[a]-fluoran
 3-n-dipentylamino-6-methyl-7-anilino-fluoran
 30 2-(4-oxo-hexyl)-3-dimethylamino-6-methyl-7-anilino-fluoran
 2-(4-oxo-hexyl)-3-diethylamino-6-methyl-7-anilino-fluoran
 2-(4-oxo-hexyl)-3-dipropylamino-6-methyl-7-anilino-fluoran

<fluorene-based leuco dyes>

35 3,6,6'-tris(dimethylamino)spiro[fluorene-9,3'-phthalide]
 3,6,6'-tris(diethylamino)spiro[fluorene-9,3'-phthalide]

<fluoran-based leuco dyes (II)>

40 2-methyl-6-p-(p-dimethylaminophenyl)aminoanilino-fluoran
 2-methoxy-6-p-(p-dimethylaminophenyl) aminoanilino-fluoran
 2-chloro-3-methyl-6-p-(p-phenylaminophenyl)-aminoanilino-fluoran
 2-chloro-6-p-(p-dimethylaminophenyl)aminoanilino-fluoran
 45 2-nitro-6-p-(p-diethylaminophenyl)aminoanilino-fluoran
 2-amino-6-p-(p-diethylaminophenyl)aminoanilino-fluoran
 2-diethylamino-6-p-(p-diethylaminophenyl)-aminoanilino-fluoran
 2-phenyl-6-methyl-6-p-(p-phenylaminophenyl)-aminoanilino-fluoran
 2-benzyl-6-p-(p-phenylaminophenyl) aminoanilino-fluoran
 50 2-hydroxy-6-p-(p-phenylaminophenyl)aminoanilino-fluoran
 3-methyl-6-p-(p-dimethylaminophenyl) aminoanilino-fluoran
 3-diethylamino-6-p-(p-diethylaminophenyl)-aminoanilino-fluoran
 3-diethylamino-6-p-(p-dibutylaminophenyl)-aminoanilino-fluoran

55 <divinyl-based leuco dyes>

3,3-bis-[2-(p-dimethylaminophenyl)-2-(p-methoxyphenyl)-ethenyl]-4, 5, 6,7-tetrabromophthalide
 3,3-bis-[2-(p-dimethylaminophenyl)-2-(p-methoxyphenyl)-ethenyl]-4,5,6,7-tetrachlorophthalide

3,3-bis-[1,1-bis(4-pyrrolidinophenyl)ethylene-2-yl]-4,5,6,7-tetrabromophthalide

3,3-bis-[1-(4-methoxyphenyl)-1-(4-pyrrolidinophenyl)-ethylene-2-yl]-4,5,6,7-tetrachlorophthalide

<Others>

1,1-bis-[2',2',2'',2''-tetrakis-(p-dimethylaminophenyl)-ethenyl]-2,2-dinitrilethane
 1,1-bis-[2',2',2'',2''-tetrakis-(p-dimethylaminophenyl)-ethenyl]-2,2-b-naphthoylethane
 1,1-bis-[2',2',2'',2''-tetrakis-(p-dimethylaminophenyl)-ethenyl]-2,2-diacetylene
 bis-[2,2,2',2'-tetrakis-(p-dimethylaminophenyl)-ethenyl]-methyl malonate dimethyl

In the present invention, as a sensitizer, an aliphatic amide such as amide stearate or amide palmitate, ethylene bisamide, montan wax, polyethylene wax, dibenzyl terephthalate, p-benzyl oxybenzyl benzoate, di-p-tolylcarbonate, p-benzyl biphenyl, phenyl α -naphthyl carbonate, 1,4-diethoxy naphthalene, 1-hydroxy-2-phenyl naphthoate, 1,2-di-(3-methylphenoxy)ethane, oxalic acid di(p-methylbenzyl), β -benzyloxynaphthalene, 4-biphenyl-p-tolyether, O-xylylene-bis-(phenylether), 4-(m-methylphenoxyethyl)biphenyl or the like may be added within the range that does not impair the effect of the invention.

In the present invention, when a plurality of reversible thermal recording layers and irreversible thermal recording layers are provided to prepare a multi-color recording medium, an intermediate layer of a resin is preferably interposed between the recording layers to be laminated together. The resin intermediate layer is intended to prevent the recording layers from being mixed together during heating and can be formed by applying a resin which does not melt at a recording temperature to the recording layers to be laminated together. The resin usable in the present invention may be of the same kind as a binder resin used in adjacent recording layers, but is preferably incompatible with the binder resin. Illustrative examples of the resin include polyvinyl alcohol, polyacrylamide, polyacrylate and polyamide resins and the like, but the resin is not limited to these. A multi-color thermal recording medium providing a vivid color tone can be obtained by providing a resin intermediate layer.

The resin intermediate layer may be thick enough not to be broken by application of heat and pressure due to repetitions of recording and erasure. If the resin intermediate layer is too thick, thermal conductivity deteriorates. Therefore, the thickness of the intermediate layer is preferably as small as possible and typically 10 μ m or less.

The intermediate layer of the present invention may contain a filler. The filler used in the invention may be an organic or inorganic filler such as silica, calcium carbonate, kaolin, baked kaolin, diatomaceous earth, talc, titanium oxide or aluminum hydroxide. The weight ratio of the filler to the resin both constituting the intermediate layer is preferably 2:1 to 20:1.

Illustrative examples of the binder used in the reversible thermal recording layer and the irreversible thermal recording layer of the present invention include denatured polyvinyl alcohols such as wholly saponified polyvinyl alcohols having a polymerization degree of 200 to 1,900, partly saponified polyvinyl alcohols, carboxy-denatured polyvinyl alcohols, amide-denatured polyvinyl alcohols, sulfonic acid-denatured polyvinyl alcohols, butyral-denatured polyvinyl alcohols and other denatured polyvinyl alcohols, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, styrene-maleic anhydride copolymer, styrene-butadiene copolymer and cellulose derivatives such as ethyl cellulose and acetyl cellulose, polyvinyl chloride, polyvinyl acetate, polyacrylamide, polyacrylate, polyvinyl butyral polystyrol and copolymers thereof, polyamide resins, silicon resins, petroleum resins, terpene resins, ketone resins and cumarone resins. These high molecular substances may be dissolved in a solvent such as water, alcohol, ketone, ester or hydrocarbon, emulsified in water or other solvent, or dispersed like a paste, and may be combined in accordance with required quality.

The filler used in the reversible thermal recording layer and the irreversible thermal recording layer of the present invention may be an organic or inorganic filler such as silica, calcium carbonate, kaolin, baked kaolin, diatomaceous earth, talc, titanium oxide and aluminum hydroxide.

In addition to these, a release agent such as an aliphatic acid metal salt, a lubricant such as wax, a water-proof agent such as glyoxal, a dispersant, an anti-foaming agent and the like can be contained in the recording layers.

Further, an overcoat layer of a high molecular substance containing a filler may be formed on a thermal color developing layer for the purpose of improving keeping quality.

Moreover, an undercoat layer containing an organic or inorganic filler may be formed under the thermal color developing layer for the purpose of improving keeping quality and sensitivity.

The above organic color developer, basic achromatic dye and materials added as required are ground with a grinder such as a ball mill, attritor or sand grinder or an appropriate emulsifier until a particle diameter of 1 μ m or less is achieved. The resulting particles are mixed with a binder and various additives according to application purpose to prepare a coating fluid.

The amounts of the organic color developer and the basic achromatic dye used in the present invention and the kinds and amounts of other components are determined according to required performance and recording quality and

not limited particularly. Typically, 1 to 8 parts of the organic color developer and 1 to 20 parts of the filler are used based on 1 part of the basic achromatic dye and 10 to 25% of the binder is used based on the total solid content.

To fabricate the reversible multi-color thermal recording medium of the present invention, the thermal coating fluid and the intermediate layer coating fluid having the above compositions are applied alternately to a desired support such as paper, synthetic paper, plastic film or nonwoven fabric and dried to prepare a multi-layered laminate. In this way, the reversible multi-color thermal recording medium of interest can be obtained.

A light absorbent which absorbs light with its thermal recording layer or the like and converts it into heat can be contained in the reversible multi-color thermal recording medium of the present invention to produce an optical recording medium. The light absorbent used in the recording medium of the present invention to convert light into heat may be any kind of substance provided it absorbs the wavelength of light coming from diverse light sources. Various dyes, various pigments, near infrared light absorbents may be used as the light absorbent of the present invention. However, the light absorbent of the present invention is not particularly limited.

When a strobe having a continuous light wavelength is used as a recording light source, for example, a product obtained from a heat reaction between a thiourea derivative and a copper compound as disclosed in Japanese Patent Publication No. 2-206583 and the specification of JP-A-5-30954, graphite, copper sulfide, lead sulfide, molybdenum trisulfide, black titanium and the like as disclosed in Japanese Patent Publication No. 3-86580 may be used as the light absorbent which converts light into heat. In addition to these, carbon black may be used as the light absorbent. These light absorbents may also be used as light absorbents for laser recording.

When a semiconductor laser which is excellent in terms of size, safety, price and modulation is used as a recording laser, particularly when a semiconductor laser having an oscillation wavelength in visible to near infrared ranges is used, examples of a material which absorbs such an oscillation wavelength include polymethine coloring matters (cyanine coloring matters), azulenium coloring matters, pyrylium coloring matters, thiopyrylium coloring matters, squale-
nium coloring matters, croconium coloring matters, dithiol metal complex salt coloring matters, mercaptophenol metal complex coloring matters, mercaptonaphthol metal complex coloring matters, phthalocyanine coloring matters, naphthalocyanine coloring matters, triallyl methane coloring matters, immonium coloring matters, diimmonium coloring matters, naphthoquinone coloring matters, anthraquinone coloring matters, metal complex salt coloring matters and the like as disclosed in JP-A-54-4142, JP-A-58-94494, JP-A-58-209594, JP-A-2-217287, Japanese Patent Publication No. 3-73814, "Near Infrared Absorbing Coloring Matters" (Chemical Industry No.43 issued in May 1986) and the like.

Illustrative examples of the polymethine coloring matters (cyanine coloring matters) include Indocyanine Green (manufactured of Daiichi Pharmaceutical Co.), NK-2014 (manufactured by Nippon Kanko Shikiso Kenkyujo Co.), NK-2612 (manufactured by Nippon Kanko Shikiso Kenkyujo Co.), 1,1,5,5-tetrakis(p-dimethylaminophenyl)-3-methoxy-1,4-pentadiene, 1,1,5,5-tetrakis (p-diethylaminophenyl)-3-methoxy-1,4-pentadiene and the like. Examples of the squalenium coloring matters include NK-2772 (manufactured by Nippon Kanko Shikiso Kenkyujo Co.) and the like. Examples of the dithiol metal complex salt coloring matters include toluene dithiol nickel complex, 4-tert-butyl-1,2-benzene dithiol nickel complex, bisdithiobenzyl nickel complex, PA-1005 (manufactured by Mitsui Toatsu Senryo Co.), PA-1006 (manufactured by Mitsui Toatsu Senryo Co.), bis(4-ethyldithiobenzyl) nickel complex disclosed in the specification of JP-A-4-80646, bis (4-n-propyldithiobenzyl)-nickel complex and the like. Examples of the immonium coloring matters and the diimmonium coloring matters include IRG002 (manufactured by Nippon Kayaku Co.), IRG022 (manufactured by Nippon Kayaku Co.) and the like. Examples of the naphthalocyanine coloring matters include NIR-4 (manufactured by Yamamoto Kasei Co.), NIR-14 (manufactured by Yamamoto Kasei Co.) and the like. Examples of the anthraquinone coloring matters include IR-750 (manufactured by Nippon Kayaku Co.) and the like. These light absorbents may be used alone or in combination of two or more.

The light absorbent used in the optical recording medium of the present invention may be simply mixed with materials required to produce the optical recording medium. However, as disclosed in Japanese Patent Publication No. 2-217287, the light absorbent is molten and mixed with materials of the light recording medium of the present invention to be dissolved or dispersed in the materials. The materials to be mixed with the light absorbent which is dissolved or dispersed therein include a sensitizer for thermal recording, the color developer of the present invention, a conventional color developer, a dye precursor, a composition comprising a sensitizer for thermal recording and the color developer of the present invention, a composition comprising a sensitizer for thermal recording and a conventional color developer, a composition comprising a sensitizer for thermal recording and a dye precursor, and the like.

As for the light absorbent used in the optical recording medium of the present invention, the materials of the optical recording medium of the present invention and the light absorbent are dissolved or dispersed in a solvent in advance, and a mixture of the dissolved or dispersed materials and light absorbent are separated from the solvent for use. The materials which are dissolved or dispersed in the solvent together with the light absorbent are the same as the above materials to be mixed with the light absorbent which is dissolved or dispersed therein.

Further, the light absorbent used in the optical recording medium of the present invention may be co-dispersed (simultaneous mixing and dispersion) with any one of a dye precursor, a color developer and a sensitizer. The light absorbent may also be co-dispersed (simultaneous mixing and dispersion) with a combination of a dye precursor and

a sensitizer or a combination of a color developer and a sensitizer.

The light absorbent used in the optical recording medium of the present invention or the light absorbent which is subjected to any one of treatments such as heat-fusion with the above materials, mixing with a solvent and co-dispersion (simultaneous mixing and dispersion) is mixed with thermal recording materials consisting of the color developer of the present invention and a dye precursor as a constituent material of a light absorptive thermal recording layer. The light absorbent may be used as a material for constituting either upper or lower light absorptive layer formed on the thermal recording layer made from the color developer of the present invention and the dye precursor. Further, the light absorbent may be used as a material for constituting both upper and lower light absorptive layers formed on both sides of the thermal recording layer. The light absorbent may be internally added to or impregnated into a support as a material for constituting the light absorptive support. On top of this light absorptive support, the above thermal recording layer or the above light absorptive thermal recording layer may be formed. The thermal recording layer or the light absorptive thermal recording layer on the light absorptive support may be multi-layer structured.

The amounts of the color developer and the dye precursor used in the reversible multi-color optical recording medium of the present invention and the types and amounts of other components are determined according to required performance and recording quality, and are not particularly limited. Typically, 1 to 8 parts of an organic color developer and 1 to 20 parts of a filler are used based on 1 part of the dye precursor and a binder is contained in an amount of 10 to 25% of the total solid content. The amount of the light absorbent added is determined according to its light absorption power.

Further, in the reversible multi-color optical recording medium of the present invention, like the thermal recording medium of the present invention, an overcoat layer of a high molecular substance or the like may be formed on the recording layer of the optical recording medium, or an undercoat layer containing an organic or inorganic filler may be interposed between the recording layer and the support for the purpose of improving keeping quality and sensitivity. The above light absorbent may be added to these overcoat layer and the undercoat layer.

The light absorbent as described above is ground with a grinder such as a ball mill, attritor and sand grinder or an appropriate emulsifier until a particle diameter of 1 μm or less is achieved and mixed with a binder and various additives according to application purpose to prepare a coating fluid.

As the light source for recording on the optical recording medium of the present invention with light, a variety of lasers such as semiconductor lasers and semiconductor excited YAG lasers, a xenon flash lamp, a halogen lamp and the like may be used. Light irradiated from these light sources may be converged with a light converging means such as a lens for optical recording on the optical recording medium of the present invention. Further, a mirror or the like may be used to carry out optical scanning recording.

Since the reversible multi-color thermal recording medium and reversible multi-color optical recording medium of the present invention have excellent heat resistance and extremely high thermal stability of its ground color, a powerful protective film can be provided by thermal lamination of a plastic film. Therefore, either before or after recording with heat or light, it is possible to easily produce a card having heat resistance and various stabilities, which is protected with a plastic film by means of a film for thermal lamination and a commercial laminator. Particularly, in the case of the optical recording medium of the present invention, additional recording with light can be made on a laminated plastic film. Illustrative examples of the plastic film for thermal lamination include thermoplastic resins such as low-density polyethylene, ethylene-vinyl acetate copolymer (EVA), ethylene-ethyl acrylate copolymer (EEA), ethylene-methyl methacrylate copolymer (EMAA) and ethylene-methacrylate copolymer (EMAA).

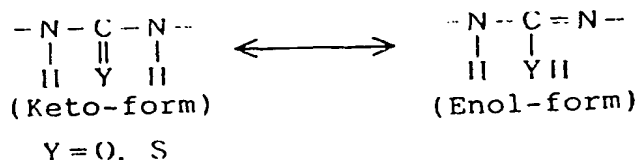
Further, extrusion coating is also possible for the reversible multi-color thermal recording medium and reversible multi-color optical recording medium of the present invention, using an extrusion coating resin such as low-density polyethylene which can be extruded at relatively low temperatures.

Moreover, since the reversible multi-color thermal recording medium and reversible multi-color optical recording medium of the present invention is excellent in heat resistance, the grounds of these media do not develop colors even if they contact a toner heat-fixing unit of an electronic photocopier. Therefore, these media can also be used as paper for electronic photocopiers. Thermal recording or optical recording is possible either before or after toner recording with an electronic photocopier.

A description is subsequently given of the mechanisms of color development and decolorization of the reversible multi-color thermal recording medium of the present invention. For instance, in the case of a reversible double-color thermal recording medium, an irreversible thermal composition comprising a basic achromatic dye (developing red color) and an irreversible heat-resistant color developer as main components, an intermediate layer, and a reversible thermal composition comprising a basic achromatic dye (developing black color) and a reversible heat-resistant color developer as main components are laminated on the support in the order named. When heat energy is applied to the reversible multi-color thermal recording medium by a thermal head, a color developing thermal reaction occurs in each layer and a mixture of black and red colors, that is, reddish black color, is obtained. On the other hand, when this color developing recording medium is subjected to heat treatment with a heated roll or thermal lamination, a decolorization reaction is instantaneously caused by the basic achromatic dye (developing black color) and the reversible heat-re-

sistant color developer. As the result, red color developed by the irreversible thermal composition remains.

Further, as for color development and decolorization, a structural change (keto-enol tautomerism) represented by the following formula may occur in the urea and thiourea derivatives of the present invention depending on conditions. It is considered that these compounds need to have an enol-form structure in order to function as color developers. To cause keto-to-enol tautomerism, high temperatures obtained by a thermal head are required and, at the same time, tautomerism to keto form occurs when an appropriate temperature and an appropriate amount of heat are given, resulting in decolorization.



Meanwhile, when a red color developing thermal recording layer, an intermediate layer and a black color developing thermal recording layer are laminated on the support in the order named, using conventional bisphenol A as a color developer, a color developing thermal reaction occurs in each layer with heat energy applied by a thermal head, and reddish black color, a mixture of black and red colors, is obtained. However, when this color developing recording medium is subjected to heat treatment with a heated roll or to thermal lamination, the hue of image portions does not change and reddish black color is markedly developed on the entire ground because bisphenol A is not a reversible heat-resistant color developer.

The reason that the urea and thiourea derivatives which are heat-resistant color developers of the present invention function as color developers for a dye precursor used in thermal recording media and optical recording media, the reason that a thermal recording medium comprising a dye precursor and the color developer of the present invention exhibits extremely high heat resistance, and the reason that an optical recording medium comprising a dye precursor, the color developer of the present invention and a light absorbent can undergo heat treatment with a heated roll or thermal lamination and exhibits extremely high heat resistance are not elucidated yet, but can be considered as follows.

In the case of the above thermal recording, since a thermal head is instantaneously heated to a temperature of 200 to 300 °C, the urea and thiourea derivatives contained in the recording layer of the thermal recording medium which is brought into contact with the thermal head undergo tautomerism to be converted into enol form and to exhibit a color developing function. It is considered that the lactone ring of the dye precursor is thereby cleaved, with the result of color development.

Further, in the case of the above optical recording, since a light absorbent is contained in the optical recording layer, light irradiated from a recording light source is absorbed efficiently and converted into heat by this light absorbent. As the temperature is elevated to 200 to 300 °C instantaneously at this point, the urea and thiourea derivatives contained in the recording layer undergo tautomerism to be converted into enol form and to exhibit a color developing function, as in the above thermal recording. It is considered that the lactone ring of the dye precursor is thereby cleaved with the result of color development.

The urea and thiourea derivatives do not exhibit a color developing function at temperatures at which they do not change into enol form. Since a reaction with the dye precursor does not occur, the color development of the ground does not take place. This seems to be the reason why heat resistance is high. The temperature at which the urea and thiourea derivatives are converted into enol form is considered to be higher than a temperature required for heat treatment with a heated roll and thermal lamination. For this reason, the color development of the ground does not take place in high-temperature thermal environment such as heat treatment with a heated roll and thermal lamination.

Further, in the case of an optical recording medium structured above and subjected to thermal lamination, light irradiated from a recording light source transmits through a plastic film present on the optical recording layer, reaches the light absorbent contained in the optical recording layer, and is converted into heat. Therefore, additional recording is possible even after lamination.

Other and further objects, features and advantages of the invention will become clear from the following description.

The present invention is further illustrated with reference to the following examples. The term "parts" used herein means "parts by weight".

<production of reversible multi-color thermal recording media: Examples 1 to 80 and Comparative Examples 1 to 10>

[Examples 1 to 20] [Examples 1' to 20']

5 Formation of irreversible thermal recording layer

Solution A (dispersion of irreversible heat-resistant color developer)

10	irreversible heat-resistance color developer (see Tables 1 and 1')	6.0 parts
	10% polyvinyl alcohol aqueous solution	18.8 parts
	water	11.2 parts

15 Solution B (dispersion of dye developing red color)

3,3-bis(1-ethyl-2-methylindole-3-yl)phthalide

2.0 parts

10% polyvinyl alcohol aqueous solution 4.6 parts

water 2.6 parts

25 The solutions having the above compositions were ground to an average particle diameter of 1 μ m with a sand grinder. Subsequently, the resulting dispersions were mixed in the proportion below to prepare a thermal layer coating fluid.

30	solution A	36.0 parts
	solution B	9.2 parts
	kaolin clay (50% dispersion)	12.0 parts

35 The above coating fluid was applied to one side of a 50 g/m² substrate in a coating weight of 5.0 g/m². The coating was then dried to form an irreversible thermal recording layer.

Formation of intermediate layer

40	kaolin clay (50% dispersion)	12.0 parts
	10% polyvinyl alcohol aqueous solution	6.0 parts
	water	3.0 parts

45 The solutions having the above compositions were mixed to prepare an intermediate layer coating fluid.

The intermediate layer coating fluid was applied to the above irreversible thermal recording layer in a coating weight of 3.0 g/m². The coating was then dried to form an intermediate layer.

Formation of reversible thermal recording layer

50 Solution D (dispersion of reversible heat-resistant color developer)

reversible heat-resistant color developer (see Tables

55

1 and 1')	6.0 parts
10% polyvinyl alcohol aqueous solution	18.8 parts
water	11.2 parts

Solution E (dispersion of dye developing black color)

3-n-dipentylamino-6-methyl-7-anilino-fluoran	2.0 parts
10% polyvinyl alcohol aqueous solution	4.6 parts
water	2.6 parts

The solutions having the above compositions were ground to an average particle diameter of 1 μ m with a sand grinder. Subsequently, the resulting dispersions were mixed in the proportion below to prepare a thermal layer coating fluid.

Solution D	36.0 parts
Solution E	9.2 parts
kaolin clay (50% dispersion)	12.0 parts

The above coating fluid was applied to the intermediate layer in a coating weight of 5.0 g/m². The coating was then dried to form a reversible thermal recording layer. This sheet was treated with a supercalender to achieve a smoothness of 600 to 700 seconds so as to prepare a reversible multi-color thermal recording sheet.

[Examples 21 to 40] [Examples 21' to 40']

Formation of reversible thermal recording layer

Solution D (dispersion of reversible heat-resistant color developer)

reversible heat-resistant color developer (see Tables 2 and 2')	6.0 parts
10% polyvinyl alcohol aqueous solution	18.8 parts
water	11.2 parts

Solution E (dispersion of dye developing black color)

3-n-dipentylamino-6-methyl-7-anilino-fluoran	2.0 parts
10% polyvinyl alcohol aqueous solution	4.6 parts
water	2.6 parts

The solutions having the above compositions were ground to an average particle diameter of 1 μ m with a sand grinder. Subsequently, the resulting dispersions were mixed in the proportion below to prepare a thermal recording layer coating fluid.

Solution D	36.0 parts
------------	------------

Continuation of the Table on the next page

(continued)

Solution E	9.2 parts
kaolin clay (50% dispersion)	12.0 parts

The above coating fluid was applied to one side of a 50 g/m² substrate in a coating weight of 5.0 g/m². The coating was then dried to form a reversible thermal recording layer.

Formation of intermediate layer

kaolin clay (50% dispersion)	12.0 parts
10% polyvinyl alcohol aqueous solution	6.0 parts
water	3.0 parts

The solutions having the above compositions were mixed to prepare an intermediate layer coating fluid.

The intermediate layer coating fluid was applied to the above reversible thermal recording layer in a coating weight of 3.0 g/m². The coating was then dried to form an intermediate layer.

Formation of irreversible thermal recording layer

Solution A (dispersion of irreversible heat-resistant color developer)

irreversible heat-resistance color developer (see Tables 2 and 2')	6.0 parts
10% polyvinyl alcohol aqueous solution	18.8 parts
water	11.2 parts

Solution F (dispersion of dye developing blue color)

3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide	2.0 parts
10% polyvinyl alcohol aqueous solution	4.6 parts
water	2.6 parts

The solutions having the above compositions were ground to an average particle diameter of 1 μm with a sand grinder. Subsequently, the resulting dispersions were mixed in the proportion below to prepare a thermal recording layer coating fluid.

Solution A	36.0 parts
Solution F	9.2 parts
kaolin clay (50% dispersion)	12.0 parts

The above coating fluid was applied to the intermediate layer in a coating weight of 5.0 g/m². The coating was then dried to form an irreversible thermal recording layer. This sheet was treated with a supercalender to achieve a smoothness of 600 to 700 seconds so as to form a reversible multi-color thermal recording sheet.

[Comparative Examples 1 to 5]

Formation of thermal recording layer

Solution G (dispersion of conventional color developer)

EP 0 709 225 A1

conventional color developer (see Table 3)	6.0 parts
10% polyvinyl alcohol aqueous solution	18.8 parts
water	11.2 parts

Solution B (dispersion of dye developing red color)

3,3-bis(1-ethyl-2-methyl-indole-3-yl)phthalide	2.0 parts
10% polyvinyl alcohol aqueous solution	4.6 parts
water	2.6 parts

The solutions having the above compositions were ground to an average particle diameter of 1 μ m with a sand grinder. Subsequently, the resulting dispersions were mixed in the proportion below to prepare a thermal recording layer coating fluid.

Solution G	36.0 parts
Solution B	9.2 parts
kaolin clay (50% dispersion)	12.0 parts

The above coating fluid was applied to one side of a 50 g/m² substrate in a coating weight of 5.0 g/m². The coating was then dried to form a thermal recording layer.

Formation of intermediate layer

kaolin clay (50% dispersion)	12.0 parts
10% polyvinyl alcohol aqueous solution	6.0 parts
water	3.0 parts

The solutions having the above compositions were mixed to prepare an intermediate layer coating fluid.

The intermediate layer coating fluid was applied to the above thermal recording layer in a coating weight of 3.0 g/m². The coating was then dried to form an intermediate layer.

Formation of thermal recording layer

Solution H (dispersion of conventional color developer)

conventional color developer (see Table 3)	6.0 parts
10% polyvinyl alcohol aqueous solution	18.8 parts
water	11.2 parts

Solution E (dispersion of dye developing black color)

3-n-dipentylamino-6-methyl-7-anilino-fluoran	2.0 parts
10% polyvinyl alcohol aqueous solution	4.6 parts
water	2.6 parts

The solutions having the above compositions were ground to an average particle diameter of 1 μ m with a sand grinder. Subsequently, the resulting dispersions were mixed in the proportion below to prepare a thermal recording layer coating fluid.

solution H	36.0 parts
solution E	9.2 parts
kaolin clay (50% dispersion)	12.0 parts

5

The above coating fluid was applied to the intermediate layer in a coating weight of 5.0 g/m². The coating was then dried to form a thermal recording layer. This sheet was treated with a supercalender to achieve a smoothness of 600 to 700 seconds so as to prepare a thermal recording sheet.

10

A quality performance test was made on the thermal recording sheets obtained in the above Examples and Comparative Examples and results are shown in Tables 1 to 3.

15

Note (1) thermal recording: Using a printer for the Rupo-90FII personal wordprocessor (manufactured by Toshiba), thermal recording was made on the reversible multi-color thermal recording media with the maximum application energy (the same conditions were also employed for thermal recording shown below). The densities of image and ground portions were measured by a Macbeth densitometer (RD-914 with an amber filter, the same conditions were employed hereinafter). Developed color tones were determined visually.

20

Note (2) decolorization (by a heated roll): The reversible multi-color thermal recording media on which dynamic recording was made by the method of Note (1) were fed through a roll heated to 115 °C at a speed of 7 mm/second and the densities of image and ground portions were measured. As for the ground portions, the smaller the Macbeth density values the more stable the color of the ground portions becomes. Contrast between image and ground portions of a thermally recorded portion which was subjected to heat treatment with a heated roll was evaluated as follows. Thermal recording media whose contrasts were rated Δ to X are difficult to read.

25

- no or almost no color development of ground portions
- Δ color development of ground portions
- X marked color development of ground portions

30

35

40

45

50

55

Note (3) thermal recording: Using a printer for the Rupo-90FII wordprocessor (manufactured by Toshiba), thermal recording was made on color undeveloped portions of reversible multi-color thermal recording media with the maximum application energy after heat treatment with a heated roll. Developed color tones were determined visually.

Table 1 Results of quality performance test

	irreversible color developer	reversible color developer	thermal recording (1)			Decolorization (with heated roll)				thermal recording (3)	
			Image portions	Ground portions	Color tone	Image portions	Ground portions	Contrast	Color tone	Image portions	Color tone
Example 1	Compound A1	Compound E6	1.30	0.04	reddish black	0.43	0.04	○	red	1.30	reddish black
Example 2	Compound A25	Compound E1	1.29	0.04	"	0.42	0.04	○	"	1.29	"
Example 3	Compound A2	Compound E2	1.30	0.04	"	0.41	0.04	○	"	1.30	"
Example 4	Compound A3	Compound E3	1.28	0.04	"	0.42	0.04	○	"	1.28	"
Example 5	Compound A4	Compound E4	1.30	0.04	"	0.40	0.04	○	"	1.30	"
Example 6	Compound A5	Compound E5	1.29	0.04	"	0.39	0.04	○	"	1.29	"
Example 7	Compound A6	Compound E7	1.31	0.04	"	0.43	0.04	○	"	1.31	"
Example 8	Compound A7	Compound E8	1.27	0.04	"	0.43	0.04	○	"	1.27	"
Example 9	Compound A8	Compound E9	1.30	0.04	"	0.45	0.04	○	"	1.30	"
Example 10	Compound A9	Compound E10	1.28	0.04	"	0.43	0.04	○	"	1.28	"
Example 11	Compound A10	Compound E1	1.27	0.04	"	0.42	0.04	○	"	1.27	"
Example 12	Compound A11	Compound E2	1.31	0.04	"	0.41	0.04	○	"	1.31	"
Example 13	Compound A12	Compound E3	1.32	0.04	"	0.43	0.04	○	"	1.32	"
Example 14	Compound A13	Compound E4	1.30	0.04	"	0.44	0.04	○	"	1.30	"
Example 15	Compound A14	Compound E5	1.29	0.04	"	0.42	0.04	○	"	1.29	"
Example 16	Compound A15	Compound E6	1.27	0.04	"	0.40	0.04	○	"	1.27	"
Example 17	Compound A16	Compound E7	1.28	0.04	"	0.39	0.04	○	"	1.28	"
Example 18	Compound A17	Compound E8	1.29	0.04	"	0.41	0.04	○	"	1.29	"
Example 19	Compound A18	Compound E9	1.30	0.04	"	0.42	0.04	○	"	1.30	"
Example 20	Compound A19	Compound E10	1.31	0.04	"	0.43	0.04	○	"	1.31	"

Table 1' Results of quality performance test

	irreversible color developer	reversible color developer	thermal recording (1)			Decolorization (with heated roll)			thermal recording (3)		
			Image portions	Ground portions	Color tone	Image portions	Ground portions	Contrast	Color tone	Image portions	Color tone
Example 1'	Compound A1	Compound E6'	1.31	0.04	reddish black	0.41	0.04	○	red	1.31	reddish black
Example 2'	Compound A25	Compound E1'	1.32	0.04	"	0.43	0.04	○	"	1.32	"
Example 3'	Compound A2	Compound E2'	1.30	0.04	"	0.44	0.04	○	"	1.30	"
Example 4'	Compound A3	Compound E3'	1.29	0.04	"	0.42	0.04	○	"	1.29	"
Example 5'	Compound A4	Compound E4'	1.27	0.04	"	0.40	0.04	○	"	1.27	"
Example 6'	Compound A5	Compound E5'	1.28	0.04	"	0.39	0.04	○	"	1.28	"
Example 7'	Compound A6	Compound E7'	1.29	0.04	"	0.41	0.04	○	"	1.29	"
Example 8'	Compound A7	Compound E8'	1.30	0.04	"	0.42	0.04	○	"	1.30	"
Example 9'	Compound A8	Compound E9'	1.31	0.04	"	0.43	0.04	○	"	1.31	"
Example 10'	Compound A9	Compound E10'	1.30	0.04	"	0.43	0.04	○	"	1.30	"
Example 11'	Compound A10	Compound E1'	1.29	0.04	"	0.42	0.04	○	"	1.29	"
Example 12'	Compound A11	Compound E2'	1.30	0.04	"	0.41	0.04	○	"	1.30	"
Example 13'	Compound A12	Compound E3'	1.28	0.04	"	0.42	0.04	○	"	1.28	"
Example 14'	Compound A13	Compound E4'	1.30	0.04	"	0.40	0.04	○	"	1.30	"
Example 15'	Compound A14	Compound E5'	1.29	0.04	"	0.39	0.04	○	"	1.29	"
Example 16'	Compound A15	Compound E6'	1.31	0.04	"	0.43	0.04	○	"	1.31	"
Example 17'	Compound A16	Compound E7'	1.27	0.04	"	0.43	0.04	○	"	1.27	"
Example 18'	Compound A17	Compound E8'	1.30	0.04	"	0.45	0.04	○	"	1.30	"
Example 19'	Compound A18	Compound E9'	1.28	0.04	"	0.43	0.04	○	"	1.28	"
Example 20'	Compound A19	Compound E10'	1.27	0.04	"	0.42	0.04	○	"	1.27	"

Table 2 Results of quality performance test

	irreversible color developer	reversible color developer	thermal recording (1)			Decolorization (with heated roll)			thermal recording (3)	
			Image portions	Ground portions	Color tone	Image portions	Ground portions	Contrast	Image portions	Color tone
Example 21	Compound B1	Compound E6	1.25	0.04	bluish black	1.01	0.04	○	1.25	bluish black
Example 22	Compound B2	Compound E11	1.24	0.04	"	1.02	0.04	○	1.24	"
Example 23	Compound B3	Compound E12	1.25	0.04	"	1.03	0.04	○	1.25	"
Example 24	Compound B4	Compound E13	1.23	0.04	"	1.03	0.04	○	1.23	"
Example 25	Compound B5	Compound E14	1.24	0.04	"	1.03	0.04	○	1.24	"
Example 26	Compound B6	Compound E15	1.26	0.04	"	1.01	0.04	○	1.26	"
Example 27	Compound B7	Compound E16	1.25	0.04	"	1.02	0.04	○	1.25	"
Example 28	Compound B8	Compound E17	1.24	0.04	"	1.00	0.04	○	1.24	"
Example 29	Compound B9	Compound E18	1.23	0.04	"	1.02	0.04	○	1.23	"
Example 30	Compound B10	Compound E19	1.24	0.04	"	1.03	0.04	○	1.24	"
Example 31	Compound B11	Compound E6	1.25	0.04	"	1.01	0.04	○	1.25	"
Example 32	Compound B12	Compound E11	1.23	0.04	"	1.01	0.04	○	1.23	"
Example 33	Compound B13	Compound E12	1.22	0.04	"	1.01	0.04	○	1.22	"
Example 34	Compound B14	Compound E13	1.21	0.04	"	1.03	0.04	○	1.21	"
Example 35	Compound B15	Compound E14	1.25	0.04	"	1.03	0.04	○	1.25	"
Example 36	Compound B16	Compound E15	1.26	0.04	"	1.02	0.04	○	1.26	"
Example 37	Compound B17	Compound E16	1.27	0.04	"	1.02	0.04	○	1.27	"
Example 38	Compound B18	Compound E17	1.26	0.04	"	1.03	0.04	○	1.26	"
Example 39	Compound B19	Compound E18	1.26	0.04	"	1.03	0.04	○	1.26	"
Example 40	Compound B20	Compound E19	1.26	0.04	"	1.01	0.04	○	1.26	"

Table 2: Results of quality performance test

	irreversible color developer	reversible color developer	thermal recording (1)			Decolorization (with heated roll)			thermal recording (3)	
			Image portions	Ground portions	Color tone	Image portions	Ground portions	Contrast	Image portions	Color tone
Example 21	Compound B1	Compound E6	1.23	0.04	bluish black	1.01	0.04	○	1.23	bluish black
Example 22	Compound B2	Compound E11	1.22	0.04	"	1.01	0.04	○	1.22	"
Example 23	Compound B3	Compound E12	1.21	0.04	"	1.03	0.04	○	1.21	"
Example 24	Compound B4	Compound E13	1.25	0.04	"	1.03	0.04	○	1.25	"
Example 25	Compound B5	Compound E14	1.26	0.04	"	1.02	0.04	○	1.26	"
Example 26	Compound B6	Compound E15	1.27	0.04	"	1.02	0.04	○	1.27	"
Example 27	Compound B7	Compound E16	1.26	0.04	"	1.03	0.04	○	1.26	"
Example 28	Compound B8	Compound E17	1.26	0.04	"	1.03	0.04	○	1.26	"
Example 29	Compound B9	Compound E18	1.26	0.04	"	1.01	0.04	○	1.26	"
Example 30	Compound B10	Compound E19	1.25	0.04	"	1.01	0.04	○	1.25	"
Example 31	Compound B11	Compound E6	1.24	0.04	"	1.02	0.04	○	1.24	"
Example 32	Compound B12	Compound E11	1.25	0.04	"	1.03	0.04	○	1.25	"
Example 33	Compound B13	Compound E12	1.23	0.04	"	1.03	0.04	○	1.23	"
Example 34	Compound B14	Compound E13	1.24	0.04	"	1.03	0.04	○	1.24	"
Example 35	Compound B15	Compound E14	1.26	0.04	"	1.01	0.04	○	1.26	"
Example 36	Compound B16	Compound E15	1.25	0.04	"	1.02	0.04	○	1.25	"
Example 37	Compound B17	Compound E16	1.24	0.04	"	1.00	0.04	○	1.24	"
Example 38	Compound B18	Compound E17	1.23	0.04	"	1.02	0.04	○	1.23	"
Example 39	Compound B19	Compound E18	1.24	0.04	"	1.03	0.04	○	1.24	"
Example 40	Compound B20	Compound E19	1.25	0.04	"	1.01	0.04	○	1.25	"

Table 3 Results of quality performance test

	conventional color developer	conventional color developer	thermal recording (1)			Decolorization (with heated roll) (2)			
			Image portions	Ground portions	Color tone	Image portions	Ground portions	Contrast	Color tone
Comparative Example 1	BPA	BPA	1.32	0.04	reddish black	1.30	1.30	x	reddish black
Comparative Example 2	BPS	BPS	1.30	0.05	"	1.30	1.30	x	"
Comparative Example 3	POB	POB	1.35	0.04	"	1.33	1.33	x	"
Comparative Example 4	D-8	D-8	1.32	0.04	"	1.30	1.30	x	"
Comparative Example 5	JK1	JK1	1.33	0.04	"	1.30	1.30	x	"

Note) Conventional color developers

BPA: bisphenol A

BPS: bisphenol S

POB: p-hydroxy benzyl benzoate

D-8: 4-hydroxy-4'-isopropoxydiphenylsulfone

JK1: 4-hydroxy-4'-butoxydiphenylsulfone

In Examples 1 to 20 and Examples 1' to 20', since a developed color tone changed from reddish black to red upon

EP 0 709 225 A1

erasure with a heated roll, the density of image portions lowered. However, stains were not observed in ground portions. The same tendency was observed in Examples 21 to 40. However, in Comparative Examples 1 to 5, there was no change in the color tone of image portions upon erasure with a heated roll, color development occurred in all the ground portions, and additional thermal recording (3) could not be made because of the absence of color undeveloped portions.

[Examples 41 to 60] [Examples 41' to 60']

Formation of irreversible thermal recording layer

Solution A (dispersion of irreversible heat-resistant color developer)

irreversible heat-resistant color developer (see Tables 4 and 4')	6.0 parts
10% polyvinyl alcohol aqueous solution	18.8 parts
water	11.2 parts

Solution I (dispersion of dye developing green color)

3-(N-p-tolyl-N-ethylamino)-7-(N-phenyl-N-methylamino)fluoran	2.0 parts
10% polyvinyl alcohol aqueous solution	4.6 parts
water	2.6 parts

The solutions having the above compositions were ground to an average particle diameter of 1 μ m with a sand grinder. Subsequently, the resulting dispersions were mixed in the proportion below to prepare a thermal recording layer coating fluid.

solution I	36.0 parts
solution G	9.2 parts
kaolin clay (50% dispersion)	12.0 parts

The above coating fluid was applied to one side of a 50 g/m² substrate in a coating weight of 5.0 g/m². The coating was then dried to form an irreversible thermal recording layer.

Formation of intermediate layer

kaolin clay (50% dispersion)	12.0 parts
10% polyacrylamide emulsion	6.0 parts
water	3.0 parts

The solutions having the above compositions were mixed to prepare an intermediate layer coating fluid.

The intermediate layer coating fluid was applied to the above irreversible thermal recording layer in a coating weight of 3.0 g/m². The coating was then dried to form an intermediate layer.

Formation of reversible thermal recording layer

Solution D (dispersion of reversible heat-resistance color developer)

reversible heat-resistant color developer (see Tables 4 and 4')	6.0 parts
10% polyvinyl alcohol aqueous solution	18.8 parts
water	11.2 parts

EP 0 709 225 A1

Solution E (dispersion of dye developing black color)

3-n-dipentylamino-6-methyl-7-anilinofluoran

2.0 parts

10% polyvinyl alcohol aqueous solution

4.6 parts

water

2.6 parts

The solutions having the above compositions were ground to an average particle diameter of 1 μ m with a sand grinder. Subsequently, the resulting dispersions were mixed in the proportion below to prepare a thermal recording layer coating fluid.

solution D	36.0 parts
solution E	9.2 parts
kaolin clay (50% dispersion)	12.0 parts

The above coating fluid was applied to the intermediate layer in a coating weight of 5.0 g/m². The coating was then dried to form a reversible thermal recording layer. This sheet was treated with a supercalender to achieve a smoothness of 600 to 700 seconds so as to prepare a reversible multi-color thermal recording sheet.

[Examples 61 to 80] [Examples 61' to 80']

Formation of irreversible thermal recording layer

Solution A (dispersion of irreversible heat-resistant color developer)

irreversible heat-resistant color developer (see Tables 5 and 5')	6.0 parts
10% polyvinyl alcohol aqueous solution	18.8 parts
water	11.2 parts

Solution J (dispersion of dye developing orange color)

3-cyclohexylamino-6-chlorofluoran

2.0 parts

10% polyvinyl alcohol aqueous solution

4.6 parts

water

2.6 parts

The solutions having the above compositions were ground to an average particle diameter of 1 μ m with a sand grinder. Subsequently, the resulting dispersions were mixed in the proportion below to prepare a thermal recording layer coating fluid.

solution A	36.0 parts
solution J	9.2 parts
kaolin clay (50% dispersion)	12.0 parts

The above coating fluid was applied to one side of a 50 g/m² substrate in a coating weight of 5.0 g/m². The coating was then dried to form an irreversible thermal recording layer. Formation of intermediate layer

kaolin clay (50% dispersion)	12.0 parts
------------------------------	------------

Continuation of the Table on the next page